

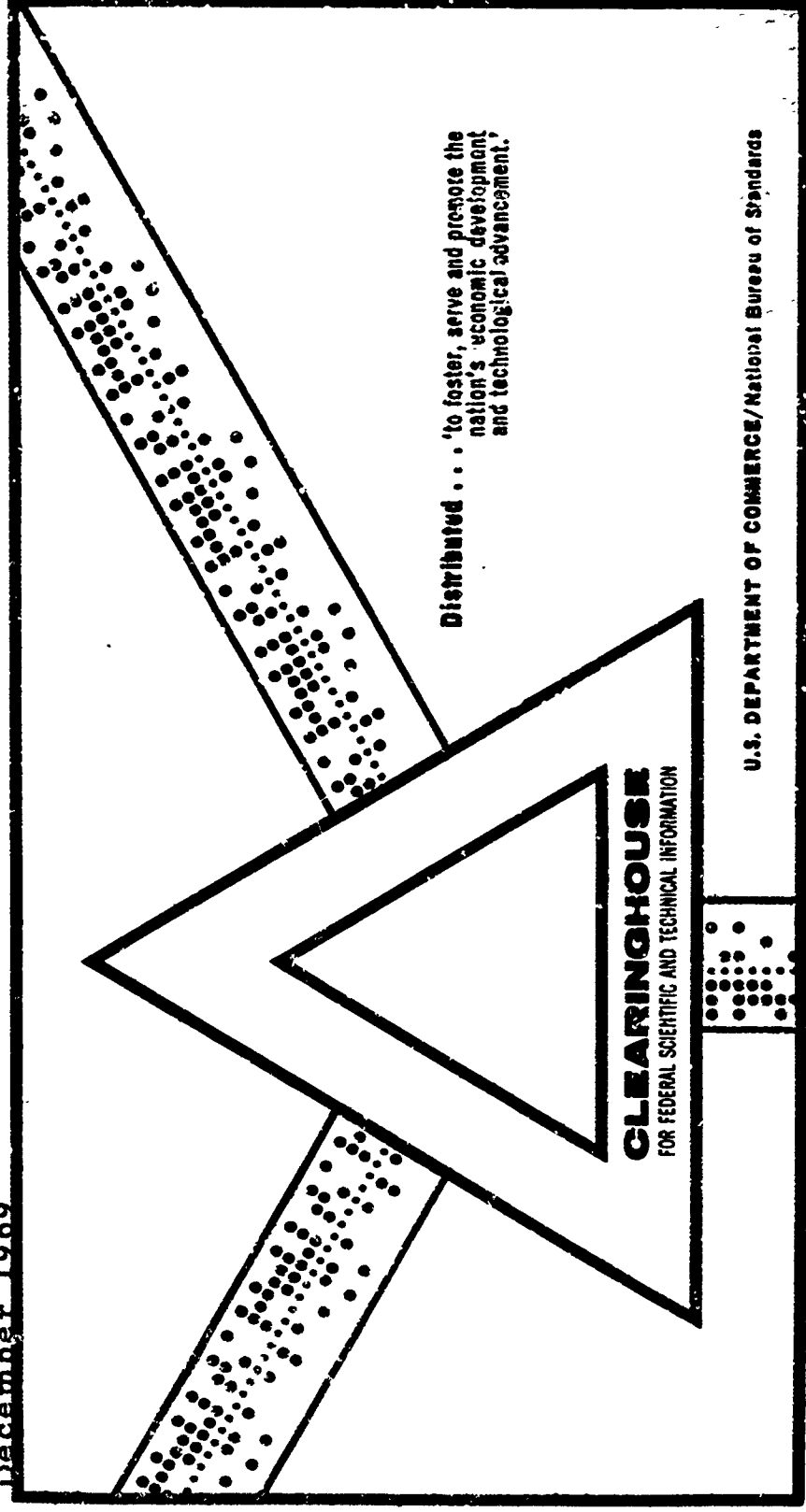
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MECHANICAL PROPERTIES OF HIGHLY FILLED ELASTOMERS VIII. RUPTURE
PROPERTIES OF THE COMPOSITE SYSTEM POLYURETHANE RUBBER-SODIUM
CHLORIDE AT ROOM TEMPERATURE

Freiedrich R. Schwarzl, et al

Central Laboratory, TNO
Delft Netherlands

December 1969



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MECHANICAL PROPERTIES OF HIGHLY FILLED ELASTOMERS VI

Rupture properties of the composite system poly-
urethane rubber-sodium chloride at room temperature

Reported by

F.R. Schwarzl and H.W. Bree

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ONR Technical Report no. 8

Mechanical Properties of Highly Filled Elastomers VIII

Rupture properties of the composite system polyurethane
rubber-sodium chloride at room temperature.

by

F.R. Schwarzl and H.W. Bree

Contribution from the Central Laboratory TNO
Delft, Netherlands

Report No. CL 69/197

Contract No. F 6/052 57 C 0059

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Delft, December 1969

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CENTRAAL LABORATORIUM TNO
DELFT

Report no.: CL 69/197
Order no. : 1507

MECHANICAL PROPERTIES OF HIGHLY FILLED ELASTOMERS VIII

Rupture properties of the composite system polyurethane
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Report by

F.R. Schwarzl and H.W. Bree

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Measurement of tensile creep
properties.

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Classification of filler substance
by sieving and air separation.

Office of Naval Research
Contract No. F 61052 67 C 0059

Delft, December 1969

Technical Report No. 8

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Summary

A large number of composites has been prepared with sodium chloride as a filler and polyurethane rubber as a binder. Two filler sizes were used, viz. a coarse filler fraction of 200 - 300 μ m and a fine filler fraction of 30 - 40 μ m. Furthermore a bimodal filler was prepared by mixing those fractions in ratios that were varied between 0,1 and 0,9 in steps of 0,1. Composites were prepared which contained between 1 vol % and 58 vol % of coarse filler, between 1 vol % and 45 vol % of fine filler, and between 40 vol % and 70 vol % of bimodal filler of different compositions.

The materials were investigated in tensile creep under dead loads at 21 °C and 65 % R.H. The creep behaviour (dewetting transition) was measured, the relationship between tensile strength and rupture time was determined, and rupture surfaces were studied.

1. INTRODUCTION

In the design of solid rocket motors, great importance is attributed to the mechanical behaviour of solid propellant grains, because presence or occurrence of cracks in the propellant during the ignition stage may lead to irregularities in the burning process and to malfunction of the rocket motor. Stress cracking in the propellant may occur during the storage period, as a result of shrinkage or of thermal stresses, or during the combustion period, because of the action of the combustion pressure or that of the acceleration forces.

For the proper understanding of the behaviour of solid propellant grains under those circumstances, detailed knowledge of the mechanical properties of highly filled elastomers is essential. The work described here was started to investigate the influence of filler characteristics, such as size, shape, content and surface treatment, on the mechanical behaviour of the filled elastomers.

To avoid complications in the preparation and handling of samples, the investigation was performed on inert filled materials. The composite propellant we have in mind consists of polyurethane rubber filled with ammonium perchlorate. The model materials investigated consisted of the same type of rubber, which, however, was filled with sodium chloride. Of course, it is realized that significant differences could exist between live and inert filled materials with respect to mechanical properties, especially to those influenced by rubber-filler interaction. It is, therefore, planned to verify general trends and conclusions found for these polyurethane - sodium chloride composites, by investigating live propellants at a later stage.

During the investigation under report, model substances were prepared on a kg-scale. Only one type of polyurethane rubber was used throughout. It was filled with various amounts of sodium chloride.

The sodium chloride filler consisted either of single fractions of the sizes 30 - 40 μm and 200 - 300 μm , or of a mixture of these fractions in various ratios.

The thermo-mechanical properties at small deformations of these model substances had earlier been investigated in dependence on temperature and frequency. A comprehensive discussion of the influence of particle size, particle size distribution and content of filler on shear moduli, thermal expansion and bulk moduli was given in preceding Technical Reports ^{1) 2) 3) 7)} and in publications ^{8) 9) 10) 11) 13)}.

The rupture properties of these model substances were investigated by measurements of tensile creep under large stresses at room temperature ^{4) 5)} and by determination of stress strain diagrams at various temperatures ⁶⁾. A discussion was given ¹²⁾ on the effect of particle size and filler content on rupture of composites with fillers of unimodal size distribution.

The work reported here was undertaken to extend these investigations to composites with fillers of bimodal size distribution. As a result of this and earlier work it seems possible now to give a general discussion on the rupture properties of the composite system (polyurethane rubber - sodium chloride) at room temperature. This will be done here. An extension of this work to other temperatures is still in progress.

2. MATERIALS

2.1. Preparation of polyurethane rubbers

All samples of filled and unfilled polyurethane rubbers prepared for tensile creep measurements, were based on a linear (polypropylene ether) glycol (Desmophen 3600^{*}) with a molecular weight of about 2,000. The molecules of this polyether were lengthened with toluene diisocyanate and crosslinked by means of trimethylol propane in the presence of a catalyst. Full details on the chemistry of the preparation of these rubbers were given in previous Technical Reports ^{1) 2) 4)}; they are not repeated here.

2.2. Survey of the materials prepared; routine control measurements

The aim of the tensile creep programme was to determine the influence of filler characteristics on the tensile creep properties of sodium chloride - polyurethane composites by systematic variation of content, particle size and particle size distribution of the filler.

A survey of the materials prepared for this tensile creep programme is given in Fig. 1 (general) and Table 1 (detailed). Polyurethane rubbers were filled with 1, 2, 5, 8, 10, 20, 30, 40, 45, 50, 55 and 57 percent by volume of coarse sodium chloride fraction no. 2 with particle size 200 - 300 μ m; furthermore polyurethane rubbers were filled with 1, 2, 5, 8, 10, 20, 25, 30, 35, 40 and 45 percent by volume of fine sodium chloride fraction no. 6 with particle size 30 - 40 μ m. Finally, a large number of polyurethane rubbers was filled with a bimodal filler substance. This filler consisted of a mixture, in different weight ratios, of coarse fraction no. 2 and fine fraction no. 6. The filler concentration of the bimodal filled materials ranged from 40 to 70 percent by volume. In Fig. 1 B, sample numbers of the bimodal filled composites are arranged according to total filler content, c, and the mixing ratio of the

^{*}) Farben Fabriken Bayer, Leverkusen, Germany.

both fractions, indicated by f , the weight ratio of the fine filler fraction in the bimodal mixture of the filler.

Fig. 1 shows that some materials were made in duplicate or triplicate. This was done to investigate the batch to batch variability, or to increase the number of specimens available for the tensile creep programme. When necessary, the surfactant Asolectin ^{*)} was used in the preparation of highly filled materials; a letter A has then been added to the sample number.

Full details about each sample are given in Table 1 ^{**) ,} pp. 39. Column 1 gives the sample number. Column 2 indicates the application of the surfactant Asolectin. (1 = Asolectin applied; 0 = no Asolectin applied) Columns 3, 4 and 5 indicate the chemical composition of the rubbery binder. Filler composition is given in columns 9 through 16 by citing the fraction number (columns 9 through 12) and their respective mixing ratios (columns 13 through 16). Plasticizer content is listed in column 17, whereas in column 18 the type of plasticizer used is indicated: "1" means diisooctylazellate.

The total filler concentration, given in columns 6, 7 and 8, was calculated from the ingredients used (column 6), as well as from the density of the composite at 23 °C (columns 7 and 8) referring to top and bottom of cured sample respectively. The values for d^{23} are given in columns 21 and 22. For the calculation we used the formula ^{2) 3) 9)}:

$$c = (d^{23} - d_r^{23}) / (d_f^{23} - d_r^{23}) \quad (1)$$

where:

*) Asolectin (Associated Concentrates Inc., New York). Filler substance treated with a solution of Asolectin in chloroform - methanol 2 : 1, followed by drying in vacuo at 40 °C.

**) Zero's in this computer composed table are used for "not determined" or "does not apply".

c = volume fraction of filler

d^{23} = density of the composite at 23 °C

d_r^{23} = density of the unfilled rubber at 23 °C = 1.067

d_f^{23} = density of the NaCl filler at 23 °C = 2.160 4) 9).

In general, the differences between the two values for the content of filler were smaller than 0.2 to 0.3 percent by volume. In the interpretation of the results, the values as calculated from the ingredients were used.

A series of very low filled samples was prepared (sample nos. 630 to 639). For these samples, optical inspection was assumed to constitute a better measure for homogeneity than the measurement of density, and the ingredients used were thought to give a better indication of the filler content than the values of the density.

The constancy of the crosslinking density of the rubbery binder over all materials prepared, was checked by measuring the swelling at equilibrium in two organic liquids, viz. chloroform and trichloroethylene. Results are given in columns 19 and 20. For the filled rubbers, the maximum relative deviations in the swelling were smaller than 7 % rel.; the standard deviation was about 3 % rel.

A series of unfilled rubbers was prepared, in which the recipe has been changed systematically to obtain rubbers with different crosslinking density, viz. swelling. These samples, numbered 479, 480, 482, 483 and 484, were used to study the influence of crosslinking density on rupture properties.

Finally four unfilled rubbers were prepared, which contained different amounts of plasticizer (sample numbers 488, 489, 490 and 491).

3. EXPERIMENTAL TECHNIQUE FOR THE DETERMINATION OF TENSILE CREEP

The principle of the measurement is explained with reference to Fig. 2. A hanging specimen in the form of a bar-bell, was subjected to a tensile stress by loading it with a constant weight. The square cross-section in the prismatic part of the specimen was about $8.0 \times 8.0 \text{ mm}^2$, and its length about 250 mm. Time-dependent tensile strain was measured by registration of the position of well-defined marks on the specimen, with regard to a precision millimeter-scale, parallel to it at a distance less than 0.5 mm.

The registration was performed automatically with an electric camera system triggered by a logarithmic clock ¹⁴⁾. Photographs were mostly made at 2, 4, 8, 16 2^k , etc. seconds after the beginning of the creep experiment. By using three marks on the specimen, at a mutual distance of 75 mm, the strain could be measured over different pieces of its prismatic part. In this way, uniformity of tensile creep over the gage length was checked. Finally, rupture time was measured by switching off a time counter by the falling weight.

For the preparation of the specimens we started from cast plates of the dimensions of $21,0 \times 150 \times 250 \text{ mm}^3$. From these, strips with a rectangular cross-section of about $9,0 \times 21,0 \text{ mm}^2$ and a length of 250 mm, were sawn. Bar-bell shaped specimens were obtained by grinding these strips. Shape and dimensions of the specimens are indicated in Fig. 3.

Lateral dimensions did not scatter more than 0,02 mm within the prismatic part of the specimen. All operations were performed on a Maximat Standard ^{*)} combined lathe and milling machine. During machining sawdust was removed with a large model vacuum cleaner.

For the measurement of samples containing 10 vol % of filler or more, brass headpieces were glued on both ends of the specimen. Suspension

^{*)} Maier & Co., Hallein, Austria.

wires were fixed on these heads. A universal joint in the stiff upper wire guaranteed a vertical position of the specimen. The thin lower wire supported the load. Contrastful circular marks were made with an elastic paint. They were defined within 0.02 mm. Precision millimeter-scales were made from "Aristo" rulers, type No. 1309/2. The sharpness of the lines turned out to be better than 0,02 mm. The scale was fixed at the upper part of the specimen by a spring construction.

When the same method was used for testing specimens of unfilled rubber, it was observed that rupture mostly occurred near the glued ends of the specimen, outside the prismatic part. Therefore special clamps were developed for testing unfilled rubbers and rubbers with a filler content lower than 10 vol %. These clamps support the specimen over the circular part between the prismatic part and the broader end of the bar-bell with two pieces of aluminium having the same radius as the circular part. The pieces are fixed between two thin metal plates in such a way that the non-prismatic part of the specimen is enclosed on all sides. A schematic representation is given in Fig. 3. Using these clamps for specimens with lower filler content, rupture always occurred within the gage length.

All measurements have been performed in a temperature and humidity conditioned room ($21 \pm \frac{1}{2}^{\circ}\text{C}$, rel. hum. $65 \pm 1\%$). For these creep experiments, the errors were less than:

- 0.2 % in the strain (absolute strain error);
- 0.1 % \pm 1 second in the elapsed time;
- 0.02 hrs in the rupture time, if it exceeded 0.1 hrs;
- \pm 2 sec. in the rupture time, if it was smaller than 0,1 hrs;
- 0.5 % in the weight (stress).

4. MEASUREMENTS

For each of the materials listed in Table 1, a number of tensile specimens was prepared and measured under various constant loads. This number varied between 3 as a minimum and 3 as a maximum. Illustrative for the results obtained, Figs. 4 and 5 show creep curves under various constant tensile loads for polyurethane rubbers containing 50 vol % of bimodal NaCl filler. Fig. 4 refers to a material with a bimodal filler which consisted of 90 % of coarse fraction no. 2 and 10 % of fine fraction no. 6.

Five specimens of this material were available; four of the specimens ruptured, as indicated by a cross in the figure. The specimen under the load of 2.5 kg/cm^2 remained still unbroken after a loading time of 10.000 hrs (longer than 1 year). The effect of the increase of tensile stress on the creep behaviour is very clearly demonstrated by Fig. 4. All creep curves start with a part of approximately time independent, small deformation. After a while a strong increase in the deformation is observed which precedes the occurrence of rupture. This increase of deformation was shown earlier to be connected to the transition of the composite from the undewetted state to the dewetted state ^{5) 12)}. The location of this transition, and that of rupture, in time scale depend strongly on the value of the load. Higher loading shifts transition and rupture to shorter times. In earlier publications ^{4) 5) 12)}, the position of the onset the dewetting transition was chosen as a basic characteristic for the discussion of the strength properties of the materials. As this transition becomes rather vague and ill-defined in time scale for materials with a lower filler content, we have chosen now the values of rupture time as a basis for the discussion of strength properties.

Fig. 5 refers to a material filled with a bimodal filler, which consisted of 80 % of coarse fraction no. 2 and 20 % of fine fraction no. 6. For these measurements, five specimens were available. The

one loaded with 3 kg/cm^2 did not break after a loading time of 1000 hrs. It was unloaded (indicated in the figure by a downward arrow) and allowed to recover for another 1000 hrs. After this time, it was reloaded with a load of 5 kg/cm^2 . It is observed that, during the second period of creep, this specimen showed deformations which were clearly too high in the beginning of the creep curve. The reason is that it was already partially dewetted during the first period of creep. The rupture point of this specimen, however, was shifted but little to shorter times and could be used within the complete series, as if it had belonged to a virginal specimen.

This procedure, of using a specimen twice, was applied a few times only. With a few exceptions, the values of the dead loads could be chosen successfully in advance to obtain rupture points which were regularly distributed in logarithmic time.

The complete set of experimental creep curves is given in Appendix I^{*)}. Each figure of this Appendix will give creep curves under various high stress levels^{**)} for one material. As symbols for fracture and unloading respectively, crosses and arrows were used.

Values of the rupture times under the various stresses are listed in Tables 2 to 9:

Table 2	unfilled unplasticized rubbers
Table 3	unfilled plasticized rubbers
Table 4	composites with coarse filler
Table 5	composites with fine filler
Table 6	composites containing 40 vol % of bimodal filler
Table 7	composites containing 50 vol % of bimodal filler
Table 8	composites containing 55 vol % of bimodal filler
Table 9	composites containing 60, 65, 67 and 70 vol % of bimodal filler.

*) Appendix I will be distributed on request.

**) In this report, tensile stress is always calculated with regard to the original cross-section of the specimen. Further, creep curves are plotted on a logarithmic time scale.

5. DISCUSSION

5.1. Rupture behaviour of unfilled polyurethane rubber

We start the discussion with the results obtained for specimens of the unfilled rubber. Fig. 6 gives creep curves at various values of the stress level for the unfilled sample no. 629. Obviously there is no considerable creep, even at stresses high enough to produce rupture. The reason for this behaviour is two-fold: the rubber was well crosslinked and the tensile creep measurements were performed at a temperature 70°C above the glass temperature of the rubber ($T_g \approx -50^{\circ}\text{C}$)¹⁰.

Though creep of the unfilled rubber is small, it is not completely absent. From the data of Fig. 6 we calculated the value of the tensile creep compliance, $F(t)$, as defined by the equation:

$$F = \epsilon / \sigma (1 + \epsilon) \quad (2)$$

In this formula we have corrected for the lateral contraction of the specimen. For all values of stress σ , compliance curves calculated from the creep curves in Fig. 6, coincide. The creep compliance may be accurately described by a straight line in double logarithmic diagram over six decades of the time scale, viz by the equation:

$$\log F(t) = a + b \log t \quad (3)$$

where F is in cm^2/kg , t is in hrs and

$$a = -1,446 \quad b = 0.0053$$

Though the compliance curves for the specimens shown in Fig. 6 agree very accurately with one another, the rupture points of those specimens show a considerable scatter. From the restricted number (8) of specimens that could be made from one batch it was impossible to obtain a reasonable impression of the rupture stress-rupture time behaviour. For this purpose a number of specimens about ten times as high would be necessary.

In order to get some information concerning the rupture behaviour of the unfilled rubber, we have plotted in Fig. 7 the rupture points of the specimens of seven unfilled samples with approximately the same value of the swelling (viz crosslinking density). Pooling all those data, it was possible to derive by statistical analysis ^{*)} the following relationship between rupture stress σ_b (in kg/cm²) and rupture time t_b (in hrs):

$$\log \sigma_b = A - B \log t_b \quad (5)$$

$$\begin{aligned} \text{with} \quad A &= 0,968 \pm 0,004 \\ \text{and} \quad B &= 0,0176 \pm 0,0039 \end{aligned} \quad (6)$$

As the coefficient of variation of the single measurement of rupture stress we found 7 %. The straight line drawn in Fig. 7 represents eq. (5). The dependence of rupture stress on rupture time is very weak. (The course of $\log \sigma$ vs $\log t$ is nearly horizontal).

The fracture surfaces of the eight specimens of sample no. 629 were studied under the microscope. From the pattern of lines on the fracture surface, it was possible to draw, with reasonable confidence, conclusions concerning the location of the origin of fracture. In six out of eight cases we observed the following fracture pattern. On the fracture surface, away from its edge, a region was found which was smoother than the remainder of the fracture surface. In this region one or more inhomogeneities were observed, very small voids in the material, from which fracture lines radiated into various directions. These fracture lines were very fine and formed a figure like a spiral. At larger distances from this point the fracture lines changed into coarser steps in the fracture surface and the picture became more rough. The pattern spreads over the entire fracture surface; mostly some of the rough steps converge towards a point situated at the opposite edge; there they become somewhat smoother again. We believe that the inhomogeneity in the interior was the origin of primary fracture, whilst the inhomogeneity at the edge

*) In the least square analysis it was assumed that rupture time was an accurately measured variable whilst rupture stress was a logarithmically normally distributed stochastic variable.

acted as an origin of a secondary fracture which was initiated during the propagation of the primary one. We do not give a micrograph but, instead a schematic drawing of two of those fracture surfaces in Figs. 8^a and 8^b. In one case we found a fracture source, which was situated at the edge; a drawing of this case is given in Fig. 8^c. In the remaining case no definite conclusions could be drawn.

From those observations we conclude that in the unfilled specimen fracture is always initiated around the stress concentration field of an inhomogeneity. This may be either a flaw or a void in the interior of the material, or a damage of the surface of the specimen, as for instance caused by the proces of machining.

The next stage in the fracture process will then be the growth of the crack until it becomes unstable. This process, which is the time determining step, is governed by the viscoelastic properties of the binder. According to a simple theoretical model by Halpin¹⁵⁾, the time dependence of strength should be connected with the creep properties of the binder by means of the equation:

$$\sigma_b = K / F (t_b / q) \quad (7)$$

In this equation, σ_b is the rupture stress, t_b the rupture time and K a parameter which is only weakly dependent on time. The time dependence of rupture stress is chiefly due to the dependence of the creep compliance, F , which is to be taken at time t_b/q , much shorter than the rupture time, t_b . It is assumed that q is a large number (between 10^4 and 10^8).

By means of equation (7) we can understand that the rupture stress of the unfilled rubber has a very weak time dependence, because the rubber shows a very weakly increasing creep curve. A direct comparison between the values of the slopes of rupture stress and creep with time in double logarithmic diagram seems to be premature. It may be sufficient to state that the values found for b in eq. (3) and B in eq. (5) are not in contradiction with the validity of eq. (7).

The weak time dependence of rupture stress also explains the large scatter in the tensile creep experiments of the unfilled samples. By this, even a moderate fluctuation in strength of the inhomogeneities will cause, a very large scatter in rupture times.

The series of unfilled rubbers with different crosslinking densities (samples nos. 479, 480, 482, 483 and 484) has also been investigated. For each of these materials, only a small number of specimens was available. Therefore, it was impossible to deduce the rupture stress - rupture time relationship independently for those samples. Instead, we assumed that also in this case a relationship of the form of eq. (5) was valid; we further assumed that only A (the value of the logarithm of strength at 1 hr), but not B (the slope) was affected by crosslinking density. Then we determined, by least square analysis, the dependence of the value of A on the crosslinking density. Results are given in Table 10. The strength is seen to increase with increasing crosslinking density (decreasing swelling).

A similar procedure was followed with regard to the series of unfilled rubbers with increasing content of plasticizer; the strength of those rubbers was found to decrease strongly with increasing plasticizer content.

Table 10 One hour tensile strength of unfilled rubbers according to eq. (5)

$$B = 0,0176$$

unplasticized; conventional value of swelling (mean of sample numbers 423, 441, 460, 478, 482, 487, 629)				
S_v (chloroform)	419	\pm	16	
S_v (tri)	319	\pm	11	
A	0,968	\pm	0,004	
σ_b , 1 hr (kg/cm ²)	9,29	\pm	7 %	
unplasticized; increasing crosslinking density				
sample no.	479	480	483	484
S_v (chloroform)	467	442	400	385
S_v (tri)	357	335	308	298
A	0,923	0,942	0,998	1,012
σ_b , 1 hr (kg/cm ²)	8,37	8,75	9,95	10,28
plasticized				
sample no.	488	489	490	491
plasticizer ^{*)} , vol. %	5,1	10,0	19,9	29,8
A	0,957	0,859	0,728	0,660
σ_b , 1 hr (kg/cm ²)	9,06	7,23	6,14	4,57

*) diisooctylazellate

5.2. Rupture behaviour of elastomers filled with coarse sodium chloride

The rupture behaviour of samples filled with coarse sodium chloride only is summarized in Figs. 9 and 10. In Fig. 9 rupture stress vs rupture time is plotted for the samples containing about 10, 20, 30, 40, 45, 50 and 55 vol % of coarse sodium chloride. Symbols of the same character are used to indicate rupture of various specimens prepared from the same batch. We observed that the scatter of the individual rupture points is not very large. Therefore it was possible to draw, with reasonable certainty, curves which represent the mean strength as function of rupture time for those materials. The lines of mean strength vs rupture time show a similar shape. In double logarithmic plot they all have a significant positive curvature, which increases slightly with increasing filler content. Therefore, for those materials the rupture time - rupture stress relationship can not be described by a simple linear equation as eq. (5). We have not tried at this stage to describe the shape of the $\sigma - t_b$ relationships by other empirical equations. Instead of that we used the drawn lines of Fig. 9 to read the values of the rupture stress corresponding with the exact rupture times of 10^{-1} , 1, 10 and 10^2 hrs. by interpolation. Sometimes, it was even possible to determine without too much extrapolation the values at the rupture times of 10^{-2} and 10^3 hrs. The corresponding stress values were listed in Table 11.

There is a strong influence of time on the rupture stress and there is a strong influence of filler content on the strength of the samples at all rupture times; the higher the filler content, the weaker the sample. From the lines of Fig. 9 we get the impression, that materials with a higher content of coarse sodium chloride show a fatigue limit, i.e. that the $\sigma_b - t_b$ relationships bend asymptotically to a horizontal level for very long times. The value of those fatigue limits decreases strongly with filler content.

The strength of the materials containing a very small amount of coarse filler, viz between 2 and 8 vol %, has been indicated in Fig. 9 by just drawing the line of mean strength without plotting the actual rupture points. It is seen that those samples show a (rupture - stress - (rupture - time) relationship, which has a smaller curvature and a more horizontal course than the higher filled samples. It resembles much more the line of mean strength vs time for the unfilled rubber which has also been drawn in Fig. 9. However, the materials containing a small amount of coarse sodium chloride are all much weaker than the unfilled rubber.

In Fig. 10 we have plotted in more detail the rupture behaviour of the materials containing 1, 2, 5, 8 and 10 vol % of coarse sodium chloride. From the position of the rupture points, we conclude that there is no significant difference between the samples containing 2, 5 and 8 vol % of sodium chloride. The rupture stress - rupture time relationship for those samples is more flat and lies above the corresponding relationship for the sample with a filler content of 10 vol %. The sample which contained 1 vol % of coarse sodium chloride differed slightly in strength from those with a filler content between 2 and 8 vol %. The reason for that is unknown.

The most striking feature of these results is the following: A material which contains a very small amount of coarse filler - in the limit just one coarse filler particle - has a strength which is about one half of the strength of the unfilled sample. This points strongly to the conclusion that the initiation of the rupture of a sample containing coarse filler must be located near the coarse filler particle. The first flaw will occur either in the vicinity of the filler particle in the binder or at the interface between filler and binder. In the first case we would have a cohesive failure of the binder initiated by the stress concentration due to the presence of the filler particle; in the latter case we would have an adhesive failure.

A decision between the two possibilities was difficult, notwithstanding the fact that we investigated by microscope a large number of fracture surfaces, especially those of materials containing a small amount of filler. We always found coarse filler particles partially sticking out of the fracture surface; those particles did not seem to be covered with a layer of rubber; we also found the replicas of the filler particles which were pulled out from the fracture surface; these replicas were negatives of the filler particles and did not show holes from parts of the binder torn out with the filler simultaneously. In no case was a fracture through the filler particles observed. The fracture surface always propagated around the filler particles, which remained unbroken. The fact that no filler particles with remainders of the binder on their surface have been detected does not prove that rupture was of the adhesive type. It is even more probable^{*)} that the process starts as a cohesive failure near the filler particle, then propagates towards the interface filler rubber, dewetting the filler particle from the binder, and finally propagates into the opposite direction through the cross-section of the specimen. In any case the result of the first step of the fracture process will be the partial dewetting of one filler particle and the occurrence of a flaw in the binder near the filler particle.

We tried to find microscopic evidence for the hypothesis that the initiation step of fracture is the dewetting of a coarse filler particle. Seven fracture surfaces of material no. 630 (1 vol % coarse filler) were investigated. We found that all fracture surfaces showed a pattern similar to that of the unfilled specimen, though it was less easy to analyze due to the disturbing effect of the presence of coarse filler particles. Two special regions on the fracture surface could be observed. One was situated in a smooth part of the fracture surface very near to one of the edges or

*) Compare 5) 12)

corners of the specimen; it was always related to a filler particle, its replica or a group of filler particles and replicas. Fine fracture lines originated from the filler particles, mostly in the shape of feathers, which connected the various filler particles in this region. We believe this region to contain the origin of primary fracture (See P in Fig. 11). At larger distances from this region the pattern became more rough and spread over the entire surface. Finally the lines converged again towards a region at the opposite edge; in this region (S) no filler particles were observed generally. Two examples are drawn in Fig. 11 a and b.

The eight fracture surfaces of material no. 638 (2 vol % of coarse filler) showed a pattern very similar to that of material 630. An example is sketched in Fig. 11 c. Fracture surfaces of the material with 5 vol % of coarse filler still showed the same pattern, however, the differences between smooth and rough parts of the fracture surface became less pronounced. The origin of fracture was always connected with a larger number of particles (10 or more). In all cases it could be traced clearly.

The fracture surfaces of the material with 8 vol % of coarse filler were much more uniform. The overall pattern did not show any longer a direction from one edge or corner to the opposite corner. However, by inspection of the four corners of the fracture surface we found that one of those corners differed from the other three. In this corner, the rubbery surface connecting the filler particles showed fine fracture lines of the shape as mentioned above. This corner contained the region of fracture initiation, which could not always be traced clearly. An example is drawn in Fig. 11 d.

Fracture surfaces of materials containing 10 volume percent of coarse filler or more were uniform and did not show any indication for the direction of propagation of fracture. No fracture lines could be detected by light microscopy ^{*)}. We found that the fracture

*) Investigations by electronmicroscopy are still to be performed.

surface of materials with a volume content higher than 10 vol % showed more roughness and irregularities than those of materials with a lower filler content.

We conclude that for materials containing less than 10 vol % of coarse filler direct microscopic evidence could be found that the initiation of fracture is connected with the presence of coarse filler particles. However, more than one filler particle seems to be involved during the stable phase of the fracture process.

The period in the fracture process following after dewetting will be the growth of the crack until it becomes unstable. A different mechanism is expected to occur during this period for rubbers with a low and a high filler content.

Consider first an elastomer with a low content of large particles. The propagating crack will then meet binder material during the major part of the time before it becomes unstable. Therefore the period of stable crack propagation will be governed by a mechanism which is similar to that of the propagation of the crack in the unfilled rubber. The only difference will be that the crack propagation occurs in a stress field which is enlarged by the stress concentration of the filler particles. We therefore expect that the rupture stress - rupture time relationships are identical for the lowly filled materials, independent of filler content, and are parallel to the rupture stress - rupture time relationship for the unfilled rubber. This is just what we observed in Figs. 9 and 10 for materials between 2 and 8 vol %.

For an elastomer filled with a higher filler content the propagating crack will not reach its unstable situation. Other filler particles will have been dewetted long before and cracks will propagate from those filler particles, some of them being situated in or near the cross-section of the first dewetted particle. Development of this process leads to an increase of the mean stress over

the remaining undewetted cross-section and will catalyze also the dewetting of other particles with a higher "dewetting strength". Finally the different propagating cracks will unite and lead to failure. It will be clear that this co-operative process ^{*)} will be much faster than the process of propagation of one single crack through the binder; it will be the faster and the more cumulative, the higher the filler content. We therefore expect the rupture stress - rupture time curves to decrease stronger with increasing rupture time, and to be shifted to shorter times and lower stresses with increasing filler content. This again is exactly the behaviour observed in Fig. 9. The change in mechanism of the second phase of fracture seems to occur between the filler contents of 8 vol % and 10 vol %.

Finally, the existence of an endurance limit for the materials with higher filler content may be interpreted as a stress limit for dewetting of the weakest of the particles of the specimen. For, in case no particle is dewetted, the process described above will not be initiated.

^{*)} This is the process which was described as dewetting of the material in ¹²⁾ and which is reflected in the dewetting transition in the creep curves.

5.3. Rupture behaviour of elastomers filled with fine sodium chloride

The rupture behaviour of samples filled with fine sodium chloride is summarized in Figs. 12 and 13. In Fig. 12 rupture stress vs rupture time is plotted for the samples containing 1, 2, 5, 8, 10 and 20 vol % of sodium chloride of the size of 30 - 40 μ m. The samples containing 1, 2 and 8 vol % of sodium chloride had about the same strength as the unfilled rubber, apart from the fact that the σ - t relationship seemed to be slightly curved for the filled samples. The sample containing 5 vol % of filler proved to be somewhat stronger; however, the rupture points of this sample showed much more scatter than the others. The sample with a filler content of 20 vol % was weaker and its σ - t relationship was more horizontal than that of the lower filled materials.

For the material with 10 vol % of filler, we only had three specimens available. The corresponding rupture points were completely out of range if compared with the result of the other materials containing fine filler. We therefore disregarded the results of samples no. 428 in the following: this in spite of the fact that we could not detect any irregularities on the corresponding fracture surfaces.

In Fig. 13 we have plotted the σ - t relationships for the samples with a higher filler content. The sample with a filler content of 25 vol % shows the maximum strength; then the strength decreases with increasing filler content. However, the sample with 45 vol % of filler seems to be stronger than those with 40 vol % of filler.

If we compare Figs. 12 and 13 with the corresponding figures for the coarse filler (Figs. 9 and 10), it is observed that the influence of filler content on strength is less for the smaller filler size; further the rupture stress is much less

dependent on rupture time for the samples with higher content of filler. Finally, a material which contains a very small amount of fine filler - in the limit just one fine filler particle - has a strength which is about equal to the strength of the unfilled material.

Therefrom we conclude that the stress concentration factor of a small filler particle will be either the same as or smaller than the stress concentration factor of the inhomogeneities which are already present in the unfilled material. We have preference for the first alternative and believe that also a small filler particle acts as a fracture source. The argument for this statement is indirect: A material with e.g. 1 vol % of small filler particles has about the same strength as the unfilled material, but the scatter in the values of the strength is much less than for the unfilled material: the artificially created fracture sources in the 1 vol % material are much less fluctuating in strength than the flaws naturally present in the unfilled rubber. The difference in scatter of the strength values between a sample containing 1 vol % of fine filler and an unfilled one can be seen by comparing the creep curves and fracture points shown in Figs. 14 and 6.

We tried to find direct evidence for the action of a small filler particle as a source for fracture initiation. However, a microscopic investigation of the fracture surface of the materials with low content of small filler particles did not succeed. Because of the optical reflection of even the smallest amount of 30 - 40 μm - particles we could not detect the pattern of the lines of fracture on the fracture surfaces with the light microscope^{*)}.

The second stage in the fracture process of materials with a

*) Investigations with the electromicroscope are still to be performed.

low content of small filler particles will be the propagation of the crack in the binder until it becomes unstable. We therefore understand why the $\sigma - t$ relationship of those materials should coincide with the $\sigma - t$ relationship of the binder.

Like in the case of large filler particles, there will be a change in mechanism of the second stage with an increase of filler content. For materials with a filler content higher than about 10 vol % considerable dewetting of the entire specimen occurs prior to rupture (ref. 12). This may be clearly seen from the strong increase of strain with time before rupture occurs. We have shown that again in Fig. 15, in which creep curves are given for materials containing various amounts of particles of small size, under a stress of 8 kg/cm^2 .

Like in the case of large particles, dewetting is accompanied by a decrease in strength; however, there is no strong change of the shape of the $\sigma - t$ relationship with increasing filler content. We do not yet understand the cause of this difference.

5.4. Rupture behaviour of highly filled elastomers

We start the discussion with the results obtained on composites with bimodal filler and very high filler content.

In Fig. 16 we have plotted rupture stress vs rupture time in a double logarithmic diagram for samples containing 60, 65, 67, and 70 volume percent of bimodal filler, composed of 30 parts of the fine and 70 parts of the coarse sodium chloride ($f = 0.3$). We observed that the scatter of the individual rupture points around the lines of mean strength was very small for highly filled elastomers. For the materials with a filler content of 65, 67 and 70 percent by volume hardly any deviation of the rupture points from the drawn lines could be detected.

Two samples with a filler content of approximately 70 vol % have been prepared and investigated, viz sample nos. 446 A and 476 A. There was a small but significant difference in the strength between these samples. In this case this difference corresponded with a difference in crosslinking density between these samples. The stronger one (sample no. 476 A) showed the lower value of the swelling in chloroform and in trichloroethylene, and therefore the higher value of crosslinking density (Compare Table 1).

This situation is typical for highly filled elastomers. The scatter of strength values of specimens from the same batch was usually very small and 4 to 5 specimens were sufficient to determine the time dependence of rupture strength of this batch over many decades in time scale. Between different batches small but significant differences in strength were observed, which could not always be explained by systematic differences in either crosslinking density, filler content or filler composition. Now and then we encountered a batch, for which the scatter of the individual specimens was much higher. A possible explanation could be that these samples have been less homogeneous than the majority of the

samples of similar composition. An example may be found in sample no. 443, as shown in Fig. 16.

In Fig. 17 we have plotted rupture stress vs rupture time for samples containing 40, 50, 55 and 60 volume percent of the same bimodal filler ($f = 0.3$). Three major differences are observed between the results presented in Figs. 16 and 17:

1. The scatter of the individual strength values of specimens of one batch is larger for the lower filled materials (Fig. 17);
2. The course of the rupture stress vs rupture time relationship is different for the lower filled and the higher filled elastomers. In the former case it is more horizontal and less curved. This is best observed by comparing the location of the rupture points of sample no. 443 (60 vol %) with the $\sigma - t_b$ relationship as drawn for the other samples in Fig. 16. Though the scatter for sample no. 443 was larger than for the other samples shown in this figure, its $\sigma - t_b$ relationship was significantly different.
3. The most important difference between Figs. 16 and 17 concerns the influence of filler content on strength. In the region of filler content between 40 vol % and 60 vol %, the strength of the filled elastomers decreases with increasing filler content, whilst from 60 vol % onwards it increases with increasing filler content. We will return to this important question in Section 5.5.

We next discuss the influence of filler composition on the strength of the bimodal filled elastomers. For this purpose we have plotted in Figs. 18, 19, 20, 21 and 22 the rupture stress vs rupture time relationships for samples containing respectively 40, 50, 55, 60 and 65 volume percent of bimodal filler of different compositions.

Consider first Fig. 18, where the rupture properties of materials with 40 vol % of filler are compared. The filler composition is

indicated by the value of f , the fraction of fine particles in the mixture of the filler. Materials shown in Fig. 18 range from $f = 0.0$ (only coarse sodium chloride) in steps of 0.1 until $f = 1.0$ (only fine sodium chloride). For a number of compositions more than one sample was prepared and investigated. Three samples have been prepared filled with 40 vol % of coarse sodium chloride, viz the samples numbered 424, 477 and 555. Those samples differed in strength. Sample no. 555 was the weakest, sample no. 424 the strongest of the three; these differences may be partially understood from minor changes in the composition and crosslinking density^{*)}. The rupture points and the line of mean strength are shown for sample no. 555 only, which was also the one prepared most recently. Differences were also found between duplicate batches with the compositions $f = 0.1$, $f = 0.2$ and $f = 0.3$. In those cases it was not easy to understand the differences by minor changes in composition or swelling. The samples with compositions $f = 0.5$, $f = 0.6$ and $f = 1.0$ were prepared in duplicate as well; here the duplicates showed good agreement in strength.

Apart from these minor fluctuations a strong influence of filler composition on strength is observed. The larger the amount of fine particles in the mixture of the filler, the higher the strength. Simultaneously, there is a systematic change of the time dependence of the strength. For the materials containing only coarse filler, the rupture stress - rupture time curves are low and show a large positive curvature; for materials containing only fine filler, the curves are higher, more horizontal and resemble much more straight lines in the double logarithmic diagram. There is a gradual change from the one shape to the other with increase of the value of f .

Similar conclusions - though less pronounced - may be drawn from the results concerning materials filled with 50 vol % (Fig. 19)

*) Sample no. 424 and 477 contained a somewhat smaller amount of filler than sample no. 555, whilst sample no. 424 showed the lowest value of the swelling.

and 55 vol % (Fig. 20) of bimodal filler.

In order to understand the rupture behaviour of bimodal filled elastomers it is of great advantage to recall a viewpoint which has been successfully used ^{7) 13)} to explain the elastic properties of the same systems. In this concept, the bimodal filled rubber is considered as a dispersion of the coarse filler particles in a hypothetical continuous matrix. This matrix then consists of the rubbery binder and the fine particles. We find for concentration, c , of the coarse particles in the total system (coarse particles + continuous matrix):

$$c' = (1 - f)c \quad (8)$$

For the concentration, c'' , of the fine particles in the continuous matrix, i.e. in the (fine particles + unfilled rubber) system, we have

$$c'' = fc / (1 - c') \quad (9)$$

We now will discuss the strength properties of the bimodal filled rubbers in terms of the concentrations c' and c'' .

In Fig. 23 we compare the $\sigma - t$ relationships for two samples which both contain the same low amount (8 vol %) of coarse particles. One of them is the sample no. 633, which does not contain any fine particles in the binder; the other is sample no. 547, which is a bimodal filled rubber with a total filler content of 40 vol % and a mixing ratio of $f = 0.8$. From eqs. (8) and (9) we find that this sample also contains 8 vol % of coarse particles which are now distributed in a matrix which itself contains 32 vol % of fine particles. The influence of the presence of fine particles in the binder on the strength is evident. The presence of the small particles has increased the strength by about 25 %.

After the discussion in the foregoing sections, the qualitative explanation of the effect of small particles is obvious. Small

particles might influence both phases of the process of fracture in the same direction. The step of initiation might be retarded: a coarse particle which is surrounded by fine particles will show a higher dewetting strength than a coarse particle in the unfilled rubber. During the second phase, i.e., the propagation of the crack through the composite binder, the fine particles will act as crack stopping inhomogeneities. Therefore also the phase of propagation of the crack is expected to be retarded by the presence of fine particles.

Fig. 23 concerned materials with a small amount of coarse particles; an even stronger effect is observed for materials with a large amount of coarse particles, as is shown in Fig. 24. In this figure we compare the $\sigma - t$ relationships for three materials which all contain the same high amount (49 - 50 vol %) of coarse particles. Sample no. 425 does not contain any fine particle in the binder. Sample no. 453 is a bimodal sample of a total filler content of 55 vol % and a mixing ratio of $f = 0,1$. This amounts to a content of 49 vol % of coarse particles, distributed in a matrix which contains 11 vol % of fine particles. As third type of material, two samples are shown of the highest filled rubber ($c = 70$ vol %; $f = 0,3$); This amounts to a content of 49 vol % of coarse particles distributed in a matrix which contains itself 41 vol % of fine particles. The large effect of the presence of fine particles in the binder is evident; the strength of the material is doubled by the presence of 41 vol % of fine particles.

It is possible to use the effect demonstrated in Fig. 24 for the prediction of the strength of highly filled rubbers containing bimodal filler from the knowledge of the strength of a composite filled with the corresponding amount (c') of coarse filler. This, however, has to be done with caution, because:

1. the curves shown in Fig. 24 do not originate one from the other by a purely vertical shift; also a small horizontal shift is involved.

2. the effect of addition of small particles to the binder depends strongly on the content of coarse particles.

This is shown in Fig. 25, where the 1 hour-strength is plotted for a number of unimodal and bimodal filled composites, using the value of c'' as abscissa and the value of c' as a parameter.

We observed that the presence of fine particles has no reinforcing effect, if no coarse particles are present (the strength decreases with increase of c'' for the curve with $c' = 0$). The reinforcing effect of fine particles is largest for a content of 50 vol % of coarse particles. In the intermediate region, (e.g. for $c' = 30$ vol %) the strength first increases with addition of fine particles, then decreases and finally increases again.

5.5. Depence of strength on filler composition and filler content

The lines of mean strength as shown in Figs. 9, 10, 12, 13, 16, 17, 18, 19, 20, 21 and 22 were used to read by interpolation the values of strength of the composites at the rupture times of 10^{-2} , 10^{-1} , 1, 10, 10^2 and 10^3 hrs. These values are listed in Table 11.

A systematic discussion of the strength of the system polyurethane rubber - sodium chloride is given with reference to Fig. 26. In this figure we have plotted the values of strength belonging to the rupture time of one hour, vs the total filler content, c, with the mixing ratio of both filler fractions, f, as a parameter. Though the picture shows some disturbing scatter, we believe to be able to draw the following general conclusions:

The unfilled rubber had a one hour strength of

$$9,3 \pm 0,6 \text{ kg/cm}^2.$$

A composite which contains a small amount of fine filler only, has about the same strength as the pure binder. If the amount of fine filler is increased beyond 25 vol %, the strength of the composite decreases.

A composite which contains a small amount of coarse filler only, has a strength which is about 60 percent of the strength of the pure binder. An increase of the amount of coarse filler beyond 10 vol % strongly decreases the strength of the composite.

A bimodal filler composed of particles of the sizes 30 - 40 μm and 200 - 300 μm is most appropriate for the preparation of composites with a high solids content, if the mixing ratio is chosen as $f = 0,3$. For those composites, the strength decreases with increasing filler content if the total filler content is below 60 vol % and increases with increasing filler content beyond 60 vol %. Composites filled with a bimodal filler with different mixing ratio show a similar behaviour; their strength also goes

through a minimum at a filler content which is somewhat below the maximum attainable loading.

If we compare the strength of the composite with $f = 0,3$ and $c = 70$ vol %, with the strength of composites with slightly different values of f and c , we arrive at an important conclusion:

The material which had been prepared to contain a solid loading as high as possible, simultaneously shows the highest value of the 1 hour strength, if compared with materials of slightly different composition.

Concerning the system polyurethane rubber - sodium chloride, we have the following data:

1. most appropriate filler composition ($30 - 40 \mu\text{m} / 200 - 300 \mu\text{m}$):
 $f = 0,3$;
2. maximum solids loading: 70 vol %;
3. one hour strength: 62 percent of the strength of the binder;
4. modulus of elasticity: 38 times the modulus of elasticity of the binder ^{*)}.

From those conclusions, only the one concerning the modulus of elasticity can be readily generalized to composites with different chemical components. The other conclusions are restricted so far to the system polyurethane rubber - sodium chloride. The conclusion about the strength is even more restricted. As the time dependence of the strength differs for materials with different filler characteristics, the picture concerning the 1000-hr strength will be slightly different from that of Fig. 26. The 1000-hr strength of the composites is plotted vs c in Fig. 27.

^{*)} This conclusion was already drawn in 7).

6. Future work

The time dependence of the strength of the composites has been discussed in this report without making use of the data available from the creep measurements during the devetting process. As an important part of the time dependence of strength will be due to the time dependence of the devetting transition in the creep curves, the relationship between both phenomena should be carefully investigated. This will be done in a subsequent technical report. For this purpose some more information is needed on the long time fatigue limits of the composites.

The conclusions drawn in this report are all restricted to room temperature. Some experimental evidence should be obtained whether the general picture of the strength of the composites remains valid at lower temperatures, where the strength of the binder will become higher with respect to the adhesion between filler and binder.

In order to apply the conclusions, obtained for the system polyurethane rubber - sodium chloride, to real propellants, some experiments are necessary to investigate the influence of the larger adhesive strength between ammonium perchlorate and binder, on the strength of the composites. In particular we intend to prepare and measure rubbers containing a very small amount of coarse and fine ammonium perchlorate particles. A similar remark holds for dummy propellants and propellants containing aluminium as a third component.

Conclusions

1. Rubbers filled with less than 10 vol % of filler do not show any creep or dewetting prior to rupture; the time determining phase in the fracture process is the propagation of the primary crack through the binder; the relationship between rupture stress and rupture time resembles that of the binder.
2. The strength of samples containing a small amount of fine filler is equal to the strength of the binder.
3. The strength of samples containing a small amount of coarse filler is about half the strength of the binder. The initiation of the primary crack was found to occur in the vicinity of coarse filler particles.
4. Composites with more than 10 vol % and less than 55 vol % of filler show a homogeneous dewetting of the material over the gage length and a dewetting transition in the creep curve prior to rupture. This dewetting is the time determining phase in the fracture process.
5. For composites with a content between 10 vol % and 55 vol % of coarse filler, the strength decreases strongly with increasing filler content; the relationship between the logarithm of tensile strength and the logarithm of rupture time becomes more curved and more time sensitive with increasing filler content.
6. For composites with a content between 25 vol % and 40 vol % of fine filler, the strength decreases with increasing filler content; the relationship between the logarithm of tensile strength and the logarithm of rupture time remains almost linear and is weakly time dependent for higher filler content.

7. Composites with more than 55 vol % of filler show inhomogeneous dewetting before rupture; only the material in the vicinity of the fracture surface is dewetted; dewetting can hardly be detected in the creep curve. The relationship between the logarithm of tensile strength and the logarithm of rupture time shows a large curvature and is strongly time dependent.
8. A bimodal filled composite may be considered as a dispersion of coarse filler particles in a hypothetical matrix, which itself consists of the binder and the fine particles. If this model is applied to the interpretation of the results, it is found that the fine particles in the binder have a strong reinforcing influence on the composite. The amount of reinforcing action, however, depends on the filler concentration of the coarse particles. Therefore, it was not possible to predict, in a simple manner, the strength of a bimodal filled composite from the strength of composites containing only coarse filler.
9. A bimodal filler composed of particles with sizes 30 - 40 μm and 200 - 300 μm is most appropriate for the preparation of highly filled elastomers, if the mixing ratio of coarse to fine material is 70 to 30. For those composites the strength decreases with increasing filler content, if the total filler content is below 60 vol %, and increases beyond this value.
10. A material which had been prepared for maximum solid loading, simultaneously has the highest value of strength, if compared with materials of only slightly different compositions.
11. The maximum loading reached was 70 vol %; the modulus of elasticity of this material was 38 times the modulus of the binder; the one-hour strength of this material was equal to 62 , of the one-hour strength of the binder.

References

1. F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers, Technical Report no. 1, Office of Naval Research, Central Laboratory TNO, Delft, July 1962.
2. F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers II, Influence of particle size and content of filler on tensile properties and shear moduli, Technical Report no. 2, Office of Naval Research, Central Laboratory TNO, Delft, April 1963.
3. F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers III, Influence of particle size and content of filler on thermal expansion and bulk moduli, Technical Report no. 3, Office of Naval Research, Central Laboratory TNO, Delft, June 1964.
4. H.W. Bree, F.R. Schwarzl and L.C.E. Struik, Mechanical Properties of Highly Filled Elastomers IV, Influence of particle size and content of filler on tensile creep at large deformations, Technical Report no. 4, Office of Naval Research, Central Laboratory TNO, Delft, July 1965.
5. L.C.E. Struik, H.W. Bree and F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers V. Influence of filler characteristics on tensile creep at large deformations, on rupture properties and on tensile strain recovery, Technical Report no. 5, Office of Naval Research, Central Laboratory TNO, Delft, April 1966.
6. C.J. Nederveen and H.W. Bree, Mechanical Properties of Highly Filled Elastomers VI. Influence of filler content and temperature on ultimate tensile properties, Technical Report no. 6, Office of Naval Research, Central Laboratory TNO, Delft, May 1967.
7. L.C.E. Struik, H.W. Bree and F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers VII The shear modulus of rubbers containing fillers with a bimodal size distribution, Technical Report no. 7, Office of Naval Research, Central Laboratory TNO, Delft, November 1967.

8. F.R. Schwarzl, H.W. Bree and C.J. Nederveen, Mechanical Properties of Highly Filled Elastomers I, Proc. 4th Int. Congr. Rheology (Providence, 1963), E.H. Lee (Ed.), Interscience/Wiley, N.Y., Vol. 3, 241-263.
9. C.W. van der Wal, H.W. Bree and F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers II, J. Appl. Polymer Sci. 9 (1965) 2143-2166.
10. F.R. Schwarzl et al, On Mechanical Properties of Unfilled and Filled Elastomers, Proc. Int. Conf. on Mech. and Chem. of Solid Propellants, Lafayette, 1965.
11. F.R. Schwarzl et al. Behaviour of Unfilled and Filled Rubbers in Shear in the Glass-Rubber Transition Region, Rheol. Acta 5 (1966) 270-275.
12. L.C.E. Struik, H.W. Bree and F.R. Schwarzl, Mechanical Properties of Highly Filled Elastomers III. Proc. Int. Rubber Conference (Brighton, 1967), MacLaren and Sons, London, 205-233.
13. F.R. Schwarzl et al, On the Rheology of Filled Elastomers, Proc. 5th Int. Congr. Rheology (Kyoto, 1968) in press.
14. L.C.E. Struik and G.A. Schwippert "Logarithmic clock, an electronic device for producing a discrete logarithmic time scale", TNO-Meios 21 (1966) 285-287.
15. J.C. Halpin "Molecular view of fracture in amorphous elastomers" Rubber Chem. Tech. 38 (1965) 1007-1038.

TABLE 1 Composition and Properties of samples investigated

SAMPLE NUMBER	COMPOSITION g/100g D3600			FILLER vol.percent calculated from			FILLER FRACTIONS						
	TDI	TMP	DB	ingr.	density		fraction numbers				mixing ratio (by weight)		
423	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
441	0	19.7	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
460	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
478	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
487	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
629	0	19.6	4.0	3.9	.0	.0	.0	0	0	0	0	0	0
479	0	17.3	3.0	2.0	.0	.0	.0	0	0	0	0	0	0
480	0	18.5	3.5	2.0	.0	.0	.0	0	0	0	0	0	0
482	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
483	0	20.7	4.5	2.0	.0	.0	.0	0	0	0	0	0	0
484	0	21.8	5.0	2.0	.0	.0	.0	0	0	0	0	0	0
488	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
489	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
490	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
491	0	19.6	4.0	2.0	.0	.0	.0	0	0	0	0	0	0
630	0	19.6	4.0	3.9	1.0	.8	1.0	2	0	0	0	0	0
634	0	19.6	4.1	3.9	1.0	1.1	.0	6	0	0	0	0	0
638	0	19.6	4.0	3.9	2.0	1.2	1.9	2	0	0	0	0	0
635	0	19.6	4.0	3.9	2.0	1.9	.0	6	0	0	0	0	0
639	0	19.6	4.0	3.9	5.0	4.1	4.7	2	0	0	0	0	0
636	0	19.6	4.0	3.9	5.0	5.0	.0	6	0	0	0	0	0
633	0	19.6	4.0	3.9	8.0	7.7	.0	2	0	0	0	0	0
637	0	19.6	4.0	3.9	8.0	8.0	.0	6	0	0	0	0	0
421	0	19.6	4.0	2.0	9.8	9.8	10.0	2	0	0	0	0	0
428	0	19.6	4.0	2.0	9.8	9.8	.0	6	0	0	0	0	0
420	0	19.6	4.0	2.0	19.7	19.4	19.8	2	0	0	0	0	0
434	0	19.6	4.0	2.0	19.7	19.6	.0	6	0	0	0	0	0
433	0	19.6	4.0	2.0	24.6	24.7	.0	6	0	0	0	0	0
422	0	19.6	4.0	2.0	29.6	29.4	29.5	2	0	0	0	0	0
431	0	19.6	4.0	1.0	29.8	29.5	.0	6	0	0	0	0	0
432	0	19.6	4.0	1.0	34.8	34.5	.0	6	0	0	0	0	0
424	0	19.7	4.0	2.0	39.5	39.4	39.5	2	0	0	0	0	0
477	0	19.6	4.0	2.0	39.5	39.5	39.6	2	0	0	0	0	0
555	0	19.6	4.0	2.0	40.0	40.3	.0	2	0	0	0	0	0
451	0	19.6	4.0	2.0	39.5	39.2	39.4	2	6	0	0	90	10
554	0	19.6	4.0	2.0	40.0	40.3	.0	2	6	0	0	90	10
477	0	19.6	4.0	2.0	39.5	39.2	39.4	2	6	0	0	80	20
553	0	19.6	4.0	2.0	40.0	40.2	.0	2	6	0	0	20	0
439	0	19.6	4.0	2.0	39.5	39.3	39.5	2	6	0	0	70	30
560	0	19.6	4.0	2.0	40.0	40.2	.0	2	6	0	0	70	30
557	0	19.6	4.0	2.0	40.0	40.3	.0	2	6	0	0	60	40
550	0	19.6	4.0	2.0	40.0	40.2	.0	2	6	0	0	50	50

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FILLER FRACTIONS								PLASTICIZER		SWELLING		DENSITY	
fraction numbers								vol. pct.	type	at equil. pct. volume increase	23 degr.C chl trl	at 23 degr.C (g/cc)	
0	0	0	0	0	0	0	0	.0	0	424	331	1.0666	.0000
0	0	0	0	0	0	0	0	.0	0	433	319	1.0672	.0000
0	0	0	0	0	0	0	0	.0	0	419	322	1.0672	.0000
0	0	0	0	0	0	0	0	.0	0	413	318	1.0648	.0000
0	0	0	0	0	0	0	0	.0	0	412	312	1.0652	.0000
0	0	0	0	0	0	0	0	.0	0	413	316	1.0652	.0000
0	0	0	0	0	0	0	0	.0	0	467	357	1.0619	.0000
0	0	0	0	0	0	0	0	.0	0	442	335	1.0652	.0000
0	0	0	0	0	0	0	0	.0	0	418	317	1.0684	.0000
0	0	0	0	0	0	0	0	.0	0	400	308	1.0705	.0000
0	0	0	0	0	0	0	0	.0	0	385	298	1.0737	.0000
0	0	0	0	0	0	0	0	5.1	1	410	308	1.0583	.0000
0	0	0	0	0	0	0	0	10.0	1	400	300	1.0510	.0000
0	0	0	0	0	0	0	0	19.9	1	395	295	1.0364	.0000
0	0	0	0	0	0	0	0	29.8	1	384	284	1.0229	.0000
2	0	0	0	0	0	0	0	.0	0	404	312	1.0732	1.0760
6	0	0	0	0	0	0	0	.0	0	370	291	1.0770	.0000
2	0	0	0	0	0	0	0	.0	0	365	283	1.0783	1.0857
6	0	0	0	0	0	0	0	.0	0	374	288	1.0858	.0000
2	0	0	0	0	0	0	0	.0	0	375	291	1.1101	1.1167
6	0	0	0	0	0	0	0	.0	0	371	289	1.1198	.0000
2	0	0	0	0	0	0	0	.0	0	375	294	1.1494	.0000
6	0	0	0	0	0	0	0	.0	0	374	289	1.1524	.0000
2	0	0	0	0	0	0	0	.0	0	428	333	1.1753	1.1770
6	0	0	0	0	0	0	0	.0	0	410	333	1.1752	.0000
2	0	0	0	0	0	0	0	.0	0	417	319	1.2812	1.2854
6	0	0	0	0	0	0	0	.0	0	406	323	1.2843	.0000
6	0	0	0	0	0	0	0	.0	0	395	306	1.3390	.0000
2	0	0	0	0	0	0	0	.0	0	422	313	1.3909	1.3927
6	0	0	0	0	0	0	0	.0	0	412	325	1.3950	.0000
6	0	0	0	0	0	0	0	.0	0	413	315	1.4469	.0000
2	0	0	0	0	0	0	0	.0	0	377	299	1.5010	1.5029
2	0	0	0	0	0	0	0	.0	0	400	309	1.5026	1.5037
2	0	0	0	0	0	0	0	.0	0	389	301	1.5066	.0000
2	6	0	0	90	10	0	0	.0	0	416	331	1.4985	1.5011
2	6	0	0	90	10	0	0	.0	0	399	314	1.5074	.0000
2	6	0	0	80	20	0	0	.0	0	400	314	1.4986	1.5020
2	6	0	0	80	20	0	0	.0	0	445	356	1.5050	.0000
2	6	0	0	70	30	0	0	.0	0	411	305	1.4998	1.5031
2	6	0	0	70	30	0	0	.0	0	389	302	1.5058	.0000
2	6	0	0	60	40	0	0	.0	0	401	305	1.5062	.0000
2	6	0	0	50	50	0	0	.0	0	391	305	1.5058	.0000

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TABLE 1 (continued)

SAMPLE NUMBER		COMPOSITION g/100g D3600			FILLER vol.percent calculated from			FILLER FRACTIONS							
		TDI	MP	DB	ingr.	density		fraction numbers				mixing ratio (by weight)			
559	0	19.6	4.0	2.0	40.0	40.2	.0	2	6	0	0	50	50	0	0
558	0	19.6	4.0	2.0	40.0	40.1	.0	2	6	0	0	40	60	0	0
548	0	19.6	4.0	2.0	40.0	39.8	40.0	2	6	0	0	30	70	0	0
547	0	19.6	4.0	2.0	40.0	39.8	40.0	2	6	0	0	20	80	0	0
546	0	19.6	4.0	2.0	40.0	40.0	40.2	2	6	0	0	10	90	0	0
436	0	19.6	4.0	1.0	39.7	39.5	.0	6	0	0	0	0	0	0	0
550	0	19.6	4.0	2.0	40.0	40.1	.0	6	0	0	0	0	0	0	0
426	0	19.6	4.0	1.0	44.8	44.3	44.6	2	0	0	0	0	0	0	0
444		19.6	4.0	1.0	44.8	44.6	.0	6	0	0	0	0	0	0	0
425		19.6	4.0	1.0	49.7	48.9	49.4	2	0	0	0	0	0	0	0
451	0	19.6	4.0	2.0	49.5	49.0	49.6	2	6	0	0	90	10	0	0
448	0	19.6	4.0	2.0	49.5	49.3	49.5	2	6	0	0	80	20	0	0
440	0	19.6	4.0	1.0	49.7	49.5	49.6	2	6	0	0	70	30	0	0
455	0	19.5	4.0	1.0	49.7	49.7	.0	2	6	0	0	60	40	0	0
458	0	19.6	4.0	1.0	49.7	49.4	49.5	2	6	0	0	50	50	0	0
465	0	19.6	4.0	1.0	49.7	49.6	49.7	2	6	0	0	40	60	0	0
463	0	19.6	4.0	1.0	49.7	49.4	49.6	2	6	0	0	30	70	0	0
473	1	19.6	4.0	2.0	49.5	48.9	49.4	2	6	0	0	20	80	0	0
427	0	19.6	4.0	.5	54.9	54.5	.0	2	0	0	0	0	0	0	0
453	0	19.6	4.0	1.0	54.8	54.5	55.3	2	6	0	0	90	10	0	0
449	0	19.6	4.0	1.0	54.8	54.1	54.5	2	6	0	0	80	20	0	0
442	0	19.6	4.0	1.0	54.8	54.5	54.6	2	6	0	0	70	30	0	0
456	0	19.6	4.0	1.0	54.8	54.5	54.6	2	6	0	0	60	40	0	0
459	0	19.6	4.0	.9	54.8	54.2	54.5	2	6	0	0	50	50	0	0
475	1	19.6	4.0	2.1	54.5	54.1	54.2	2	6	0	0	40	60	0	0
474	1	19.6	4.0	2.0	54.5	53.6	54.3	2	6	0	0	30	70	0	0
437	1	19.6	4.0	.9	56.9	56.8	53.8	2	0	0	0	0	0	0	0
469	1	19.6	4.0	2.0	59.6	58.9	59.5	2	6	0	0	90	10	0	0
450	0	19.6	4.0	2.0	59.6	59.5	59.7	2	6	0	0	80	20	0	0
443	0	19.7	4.0	1.1	59.8	59.2	59.5	2	6	0	0	70	30	0	0
471	1	19.6	4.0	2.0	59.6	59.4	59.6	2	6	0	0	60	40	0	0
468	1	19.6	4.0	2.0	59.6	59.2	59.3	2	6	0	0	50	50	0	0
467	1	19.6	4.0	2.0	64.6	64.4	64.5	2	6	0	0	80	20	0	0
445	1	19.6	4.0	1.0	64.8	64.3	64.7	2	6	0	0	70	30	0	0
472	1	19.6	4.0	2.1	64.5	64.2	64.4	2	6	0	0	60	40	0	0
470	1	19.6	4.0	2.1	67.1	66.6	66.9	2	6	0	0	70	30	0	0
446	1	19.6	4.0	2.0	69.6	68.3	69.5	2	6	0	0	70	30	0	0
476	1	19.8	4.0	2.0	69.6	69.2	69.5	2	6	0	0	70	30	0	0

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FILLER FRACTIONS								PLASTICIZER		SWELLING		DENSITY	
fraction numbers				mixing ratio (by weight)				vol. pct.	type	at equil. pct. volume increase		at 23 degr.C (g/cc)	
										23 degr.C chl tri			
2	6	0	0	50	50	0	0	.0	0	389	305	1.5052	.0000
2	6	0	0	40	60	0	0	.0	0	388	303	1.5049	.0000
2	6	0	0	30	70	0	0	.0	0	401	314	1.5015	1.5040
2	6	0	0	20	80	0	0	.0	0	401	316	1.5022	1.5032
2	6	0	0	10	90	0	0	.0	0	375	290	1.5042	1.5057
6	0	0	0	0	0	0	0	.0	0	403	322	1.5024	.0000
6	0	0	0	0	0	0	0	.0	0	378	298	1.5050	.0000
2	0	0	0	0	0	0	0	.0	0	420	326	1.5553	1.5582
6	0	0	0	0	0	0	0	.0	0	428	311	1.5580	.0000
2	0	0	0	0	0	0	0	.0	0	419	323	1.5058	1.6117
2	6	0	0	90	10	0	0	.0	0	408	316	1.6074	1.6135
2	6	0	0	80	20	0	0	.0	0	405	318	1.6095	1.6125
2	6	0	0	70	30	0	0	.0	0	412	324	1.6124	1.6134
2	6	0	0	60	40	0	0	.0	0	412	327	1.6150	.0000
2	6	0	0	50	50	0	0	.0	0	417	332	1.6113	1.6131
2	6	0	0	40	60	0	0	.0	0	421	315	1.6137	1.6145
2	6	0	0	30	70	0	0	.0	0	414	309	1.6110	1.6136
2	6	0	0	20	80	0	0	.0	0	397	303	1.6056	1.6105
2	0	0	0	0	0	0	0	.0	0	421	331	1.5665	.0000
2	6	0	0	90	10	0	0	.0	0	416	330	1.6674	1.6764
2	6	0	0	80	20	0	0	.0	0	422	335	1.6634	1.6672
2	6	0	0	70	30	0	0	.0	0	405	316	1.6675	1.6669
2	6	0	0	60	40	0	0	.0	0	411	322	1.6669	1.6690
2	6	0	0	50	50	0	0	.0	0	419	322	1.6643	1.6679
2	6	0	0	40	60	0	0	.0	0	398	308	1.6634	1.6641
2	6	0	0	30	70	0	0	.0	0	395	307	1.6582	1.6611
2	0	0	0	0	0	0	0	.0	0	408	300	1.6924	1.7146
2	6	0	0	90	10	0	0	.0	0	375	299	1.7147	1.7239
2	6	0	0	80	20	0	0	.0	0	394	315	1.7228	1.7243
2	6	0	0	70	30	0	0	.0	0	410	309	1.7190	1.7232
2	6	0	0	60	40	0	0	.0	0	390	303	1.7209	1.7225
2	6	0	0	50	50	0	0	.0	0	413	327	1.7191	1.7203
2	6	0	0	80	20	0	0	.0	0	387	305	1.7753	1.7774
2	6	0	0	70	30	0	0	.0	0	405	308	1.7752	1.7786
2	6	0	0	60	40	0	0	.0	0	388	298	1.7736	1.7762
2	6	0	0	70	30	0	0	.0	0	411	317	1.7995	1.8033
2	6	0	0	70	30	0	0	.0	0	408	299	1.8194	1.8322
2	6	0	0	70	30	0	0	.0	0	377	290	1.8278	1.8317

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Table 2 Rupture times, in hrs, of samples of unfilled polyurethane rubbers

samples no. swelling in chloroform	423	441	460	478	487	629	479	480	482	483	484
in trichloro ethylene	424	433	419	413	412	413	467	442	418	400	385
no. of specimens	331	319	322	318	312	316	357	335	317	308	298
	5	5	5	5	5	8	4	5	4*)	5	5
load, kg/cm ²											
7,75						1,69					
8,0					910	4,2; 100; 330	0,04; 35,5				
8,5					0,035	7,80	2,5	0,29; 0,48			
8,75								2,00			
9,0	0,02		0,035; 0,04			3,50	0,12	3,90	2,60	5,40	475
9,25		104	1,73	0,17; 0,60							
9,38					2,20						
9,5	0,015; 0,62	3,15	0,11	28,0		0,69		0,07	0,62	2,50	11,0
10,0	1,55	1,55	0,015	0,23	0,18				0,17	2,10	1,35
10,5	0,007	0,48		0,06	0,03	0,37				1,66	1,45
11,0		0,01								0,015	0,42

*) One specimen showed a void in the fracture surface; the corresponding measurement was rejected

Table 3 Rupture times, in hrs, of samples of unfilled plasticized polyurethane rubbers

sample no. plast. vol % no. of specimens	487	488	489	490	491
stress, kg/cm ²					
4,0					180
4,5					0,064
5,5				4,5: 1800	0,012
6,0				22	
6,5			33	0,017	
7,0			0,17	0,011	
7,5			0,33		
8,0	910	350	0,015		
8,5	0,035	0,22			
9,59			0,0026		
9,0		2,30			
9,38	2,20				
9,5					
10,0	0,18	0,10			
10,3		0,016			
10,5	0,03				

table 4 Rupture times, in hrs, of samples containing NaCl filler of size 210 - 300 μ m

filler content sample no. no. of specimens	1%	2%	5%	8%	10%	20%	30%	40%	40%	45%	50%	55%	57%
1,6	630	638	639	633	421	420	422	424	477	426	425	427	437A
2,0	7	8	8	7	5	4	5	3	5	4	3	4	5
2,5													
2,7													
2,75													
3,0													
3,5													
4,0													
4,2													
4,5	23	1200	1819	1250									
4,75			32; 145	50,1									
5,0	0,15; 4,80	0,78; 0,93; 11,0	6,20	21									
5,5	0,33	0,15; 0,36	1,25	0,38; 1,0									
6,0	0,11	0,30	0,15	0,20									
6,5		0,015	0,046	0,021									
7,0	0,025		0,006										
stress, kg/cm ²													
1,6													
2,0													
2,5													
2,7													
2,75													
3,0													
3,5													
4,0													
4,2													
4,5													
4,75													
5,0													
5,5													
6,0													
6,5													
7,0													

Table 5 Rupture times, in hrs, of samples containing NaCl filler of size 33 - 40 μ m

filler content sample no.	1%	2%	5%	8%	10%	20%	25%	30%	35%	40%	40%	45%
no. of specimens	674	635	636	637	428	434	433	431	432	436	556	444A
	8	8	7	8	4	5	5	5	4	4	5 ^{*)}	5
stress, kg/cm ²												
6					.					50	235	165
6,5					0,33							
7,0					0,30				250	1,90	2,00	1,75
7,5						310	730	120	19,5	0,18		0,66
7,75 ; 7,8	1500					100						
8,0	275			.	0,051	0,40	56	45	0,96	0,06	0,08	0,18
8,25 (8,3)		0,59; 4,2		(0,015)								
8,5	8,2	46		2,1; 31		0,044		0,15			0,025	0,07
8,75			5,0									
9,0	2,1	0,12; 2,1	210	3,40		0,026	1,21	0,18	0,028			
9,5	0,43	0,24	0,84; 1,1	4,60			0,036	0,017				
10,0	0,06	0,07	2,5	0,53			0,017					
10,5	0,018	0,05	0,004									
11,0	0,0037		0,06	0,011								
11,5												
12,0												

*1) One specimen showed a void in the fracture surface; the corresponding measurement was rejected.

Table 6 Rupture times, in hrs, of samples containing 40 vol % bimodal NaCl filler of various compositions

sample no.	424	477	555	451	554	447	553	430	560	557	550	559	549	558	548	547	546	436	556
f	0	0	0	0,1	0,1	0,2	0,2	0,3	0,3	0,4	0,5	0,5	0,5	0,6	0,7	0,7	0,9	1,0	1,0
no. of specimens	3	5	5	4	5	4	5	4	5	5	5	6	5	5	5	5	5*	4	5*
load, kg/cm ²																			
2,5																			
2,75			121																
3,0		18,2	4,08																
3,5	5,55	2,55		230	18,33	2730		44											
3,75									22,30										
4,0	0,89	0,19	0,13	10	0,96	20,2	240	10	125			895							
4,5				1,24		1,35	20,00	1,03	12,31	9,75									
4,8																			
5,0	0,03	0,003	0,008	0,22	0,055	0,33	1,05	0,28	0,82	0,59	125	26,33	202	80	914				
5,3											69,7								
5,5					0,008					0,17	5,55	0,17	8,52	4,30	101	1205			
5,75																			
6,0							0,075		0,03	0,034	0,70	0,22	2,55	0,34	2,92	1744	65,5	50	235
6,5							0			0,015		0,072	0,28	0,11					
7,0											0,03	0,017	0,05	0,03	0,09	0,45	0,42	1,90	1,99
7,5															0,03			0,18	
8,0																0,038	0,032	0,06	0,08
8,5																0,02			0,025

*) One specimen showed a void in the fracture surface; the corresponding measurement was rejected.

Table 7 Rupture times, in hrs, of samples containing 50 vol % bimodal NaCl filler of various compositions

sample no.	425	452	448	440	455	458	465	463	473A
f	0	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8
no. of specimens	3	5	5	5	5	4	4	5	5
load, kg/cm ²									
2,0	580								
2,5	2,5	.							
3,0	0,16	78							
3,5		1,70	555	640	1000				
4,0		0,22	8,9	34,5	50	95	900		
4,5		0,02	1,62	2,40	2,50	7,0	18	920	1250
5,0			0,08	0,42	0,285	0,66	1,22	13,2	110
5,5			0,03	0,04	0,06	0,11	0,30	1,52	12,5
6,0								0,27	2,30
6,5									
7,0								0,036	0,30

Table 9 Rupture times, in hrs, of samples containing bimodal NaCl filler

filler content		60 vol %						65 vol %			67 vol %	70 vol %	
sample no.		469A	450	443	471A	468A	467A	445A	472A	470A	446A	476A	
f		0,1	0,2	0,3	0,4	0,5	0,2	0,3	0,4	0,3	0,3	0,3	
no. of specimens		5	4	5	5	4	4	4	4	5	5	6*)	
load, kg/cm ²													
2,5	44												
3,0	3,25		740	700			155	220					
3,5	0,62		10,5	11,0	85					96			
4,0	0,21		2,20	0,63	11,5	31,0	2,79	2,50	37	22	70		
4,5				0,35								20	
5,5	0,03		0,07	0,056	0,60	1,70	0,33	0,20	3,20	0,59	2,55	1,65	
6,0					0,068	0,17	0,06	0,04	0,36	0,13	0,33	0,32	
6,5													
7,0					0,015	0,042			0,06		0,072	0,06	
7,5										0,015			
8,0											0,022		

*) Two specimens showed a void in the fracture surface; the corresponding data were rejected.

Table 11 Tensile strength, in kg/cm^2 , of composites as function of rupture time, in hrs.

Sample no.	filler content*) vol %	filler composition f	tensile strength, σ after (hrs)					
			10^{-2}	10^{-1}	10^0	10^1	10^2	10^3
630	1,0	0,0	-	6,05	5,3	4,8	4,5	4,27
634	1,0	1,0	10,9	9,85	9,1	8,6	8,25	8,0
638	2,0	0,0	6,9	6,1	5,5	5,0	4,7	4,6
635	2,0	1,0	10,9	9,85	9,1	8,6	8,25	8,0
639	5,0	0,0	6,9	6,1	5,5	5,0	4,7	4,6
636	5,0	1,0	-	10,5	9,8	9,25	8,85	8,55
633	8,0	0,0	6,9	6,1	5,5	5,0	4,7	4,6
637	8,0	1,0	10,9	9,85	9,1	8,6	8,25	8,0
421	9,8	0,0	6,8	5,65	4,85	4,25	3,9	3,65
428	9,8	1,0	-	-	-	-	-	-
420	19,7	0,0	6,5	5,4	4,65	4,1	3,65	3,5
434	19,7	1,0	9,2	8,4	7,9	7,75	7,65	7,6
433	24,6	1,0	10,2	9,55	9,0	8,45	7,95	7,5
422	29,6	0,0	-	4,7	4,0	3,5	3,2	3,07
431	29,8	1,0	9,65	9,05	8,55	8,05	7,6	7,15
432	34,8	1,0	9,2	8,6	8,1	7,65	7,2	6,75
424	39,5	0,0	-	4,5	3,9	3,4	3,1	2,96
477	39,5	0,0	-	4,2	3,55	3,1	2,85	2,72
555	40,0	0,0	4,9	4,0	3,4	2,95	2,7	2,6
451	39,5	0,1	-	5,2	4,5	4,0	3,6	3,45
554	40,0	0,1	5,6	4,65	4,0	3,5	3,25	3,05
447	39,5	0,2	-	5,4	4,6	4,1	3,75	3,6
553	40,0	0,2	7,15	5,9	5,10	4,55	4,15	3,95
439	39,5	0,3	-	5,3	4,55	4,05	3,7	3,5
560	40,0	0,3	-	5,8	4,9	4,4	4,0	3,8
557	40,0	0,4	6,9	5,7	4,85	4,35	4,1	3,9
550	40,0	0,5	7,6	6,6	5,9	5,4	5,05	4,85
559	40,0	0,5	7,3	6,3	5,6	5,15	4,75	4,5
558	40,0	0,6	7,45	6,5	5,8	5,35	5,0	4,77
548	40,0	0,7	8,05	7,0	6,3	5,8	5,5	5,3
547	40,0	0,8	8,65	7,55	6,75	6,15	5,8	5,55
546	40,0	0,9	8,7	7,65	6,9	6,3	5,9	5,7

*) As calculated from ingredients

Table 11 (continued) Tensile strength, in kg/cm^2 , of composites as function of rupture time, in hrs.

Sample no.	filler content*) vol %	filler composition f	tensile strength, σ after (hrs)					
			10^{-2}	10^{-1}	10^0	10^1	10^2	10^3
436	39,7	1,0	-	7,85	7,05	6,4	5,9	5,6
556	40,0	1,0	8,85	7,9	7,15	6,55	6,1	5,9
426	44,8	0,0	-	3,55	2,95	2,6	2,35	2,25
444 A	44,8	1,0	-	8,15	7,3	6,65	6,15	5,85
425	49,7	0,0	-	3,25	2,65	2,3	2,08	1,99
452	49,5	0,1	4,95	4,15	3,6	3,2	2,96	2,76
448	49,5	0,2	6,0	5,15	4,5	4,0	3,65	3,4
440	49,7	0,3	6,2	5,3	4,65	4,15	3,75	3,45
455	49,7	0,4	-	5,35	4,75	4,25	3,85	3,55
458	49,7	0,5	-	5,55	4,9	4,4	3,95	3,7
465	49,7	0,6	-	5,8	5,1	4,6	4,2	3,95
463	49,7	0,7	7,9	6,45	5,55	5,0	4,65	4,45
473 A	49,5	0,8	-	7,75	6,35	5,55	5,05	4,7
427	54,9	0,0	-	2,95	2,45	2,05	1,85	1,74
453	54,8	0,1	-	3,85	3,25	2,80	2,55	2,35
449	54,8	0,2	-	4,40	3,70	3,2	2,85	2,6
442	54,8	0,3	-	5,40	4,65	4,10	3,70	3,48
456	54,8	0,4	-	5,2	4,50	3,95	3,60	3,40
459	54,8	0,5	-	5,85	5,0	4,45	4,0	3,70
475 A	54,5	0,6	-	6,35	5,35	4,7	4,2	3,85
474 A	54,5	0,7	-	7,05	5,85	5,05	4,5	4,15
437 A	56,9	0,0	-	3,8	2,9	2,32	1,93	1,66
469 A	59,6	0,1	5,7	4,25	3,40	2,8	2,4	2,18
450	59,6	0,2	5,85	4,9	4,2	3,7	3,35	3,05
443	59,8	0,3	6,15	5,0	4,15	3,6	3,2	2,95
471 A	59,6	0,4	7,45	5,8	4,7	4,0	3,5	3,22
468 A	59,6	0,5	8,1	6,3	5,15	4,35	3,85	3,51
467 A	64,6	0,2	-	5,9	4,5	3,65	3,1	2,68
445 A	64,8	0,3	7,0	5,4	4,4	3,7	3,15	2,77
472 A	64,5	0,4	-	6,75	5,4	4,45	3,85	3,4
470 A	67,1	0,5	7,9	6,10	4,95	4,15	3,55	3,15
446 A	69,6	0,3	8,9	6,75	5,45	4,55	3,95	3,56
476 A	69,6	0,3	9,6	7,15	5,7	4,75	4,1	3,7

*) As calculated from ingredients

Legend to figures

- Fig. 1. Survey of the materials prepared and investigated for tensile creep properties.
- Fig. 2. Schematic illustration of the tensile creep measurement for specimens from filled materials.
- Fig. 3. Clamping of specimen from unfilled rubber and dimensions of the tensile creep specimen.
- Fig. 4. Tensile creep curves for various stress levels for bimodal filled polyurethane rubber no. 452 containing 49,5 vol % of bimodal filler with a filler composition $f = 0,1$; temp. 21°C ; R.H. 65 %.
- Fig. 5. Tensile creep curves for various stress levels for bimodal filled polyurethane rubber no. 448 containing 49,5 vol % of bimodal filler with a filler composition $f = 0,2$; temp. 21°C ; R.H. 65 %.
- Fig. 6. Tensile creep curve for various stress levels for unfilled polyurethane rubber 629; temp. 21°C ; R.H. 65 %.
- Fig. 7. Tensile stress vs rupture time for various unfilled polyurethane rubbers as indicated. The drawn line represents eq. (5).
- Fig. 8. Schematic drawings of the rupture surface of three specimens from unfilled rubber 629, broken in tensile creep.
- Fig. 9. Tensile stress vs rupture time for various rubbers filled with different amounts of coarse sodium chloride fraction no. 2 (200 - 300 μm) as indicated; also shown are the lines of mean strength for the unfilled rubber and for samples containing a small amount of filler fraction no. 2; temp. 21°C ; R.H. 65 %.

Fig. 10. Tensile stress vs rupture time for various rubbers filled with a small amount of filler fraction no. 2 (200 - 300 μm) as indicated; also shown are the lines of mean strength for the unfilled rubber and for the sample containing 10 vol % of filler fraction no. 2; 21 $^{\circ}\text{C}$; R.H. 65 %.

Fig. 11. Schematic drawings of rupture surfaces of specimen from polyurethane rubber containing small amounts of coarse sodium chloride fraction no. 2 (200 - 300 μm).

11a and 11b rupture surface of tensile specimen from polyurethane rubber no. 630, containing 1 vol % of coarse filler.

11c rupture surface of tensile specimen from polyurethane rubber no. 638, containing 2 vol % of coarse filler.

11d rupture surface of tensile specimen from polyurethane rubber no. 633, containing 8 vol % of coarse filler; drawing shows a magnification of a part of the surface where, probably, the primary origin of rupture was situated.

Fig. 12. Tensile stress vs rupture time for various rubbers filled with different amounts of filler fraction no. 6 (30 - 40 μm), as indicated.

Fig. 13. Tensile stress vs rupture time for various rubbers filled with different amounts of filler fraction no. 6 (30 - 40 μm), as indicated.

Fig. 14. Tensile creep curves for various stress levels for polyurethane rubber no. 634, filled with 1 vol % of filler fraction no. 6 (30 - 40 μm); temp. 21 $^{\circ}\text{C}$; R.H. 65 %.

Fig. 15. Tensile creep curves, under a stress of 8 kg/cm^2 for polyurethane rubbers filled with different amounts of filler fraction no. 6 (30 - 40 μm); temp. 21 $^{\circ}\text{C}$; R.H. 65 %.

Fig. 16. Tensile stress vs rupture time for various rubbers filled with high amounts of binodal sodium chloride filler with composition $f = 0,5$; temp. 21 $^{\circ}\text{C}$; R.H. 65 %.

- Fig. 17. Tensile stress vs rupture time for various rubbers filled with different amounts of bimodal sodium chloride filler with composition $f = C,3$; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 18. Tensile stress vs rupture time for rubbers filled with approximately 40 vol % of bimodal sodium chloride filler of various compositions; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 19. Tensile stress vs rupture time for rubbers filled with approximately 50 vol % of bimodal sodium chloride filler of various composition: temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 20. Tensile stress vs rupture time for rubbers filled with approximately 55 vol % of bimodal sodium chloride filler of various compositions; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 21. Tensile stress vs rupture time for rubbers filled with approximately 60 vol % of bimodal sodium chloride filler of various compositions; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 22. Tensile stress vs rupture time for rubbers filled with approximately 65 vol % of bimodal sodium chloride filler of various compositions; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 23. Tensile stress vs rupture time for two rubbers containing approximately 8 vol % of coarse particles, with a different content of fine particles; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 24. Tensile stress vs rupture time for three materials containing approximately 50 vol % of coarse particles, with a different content of fine particles; temp. $21^{\circ}C$; R.H. 65 %.
- Fig. 25. One-hour strength plotted vs c'' , the volume content of fine particles in the binder, with c' , the volume content of coarse particles as a parameter.

Fig. 26. One-hour strength plotted vs c , the total filler content, with f , the mixing ratio of the bimodal filler, as a parameter. Also shown is the one-hour strength of the binder.

Fig. 27. 1000-hrs strength plotted vs c , the total filler content, with f , the mixing ratio of the bimodal filler, as a parameter. Also shown is the 1000-hrs strength of the binder.

Fig.1A Tensile creep programme unimodal filled rubbers									
c.vol.% NaCl	1%	2%	5%	8%	10%	20%	25%	30%	35%
33-40 μm	634	635	636	637	428	434	433	431	432
210-300 μm	630	638	639	633	421	420		422	

Fig.1B Tensile creep programme bimodal filled rubbers													
Mixing ratio 33-40 / 210-300 μm													
c.vol.% NaCl	0/100	10/90	20/80	30/70	40/60	50/50	60/40	70/30	80/20	90/10	100/0		
40%	424,477 555	451,554	447,553	439,560	557	559,550	549,558	548	547	546	436,556		
45%	426										444A		
50%	425	452	448	440	455	458	465	463	473A				
55%	427	453	449	442	456	459	475A	474A					
57%	437A												
60%		469A	450	443	471A	468A							
65%			467A	445A	472A								
67%				470A									
70%				446A 473A									
f	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0		

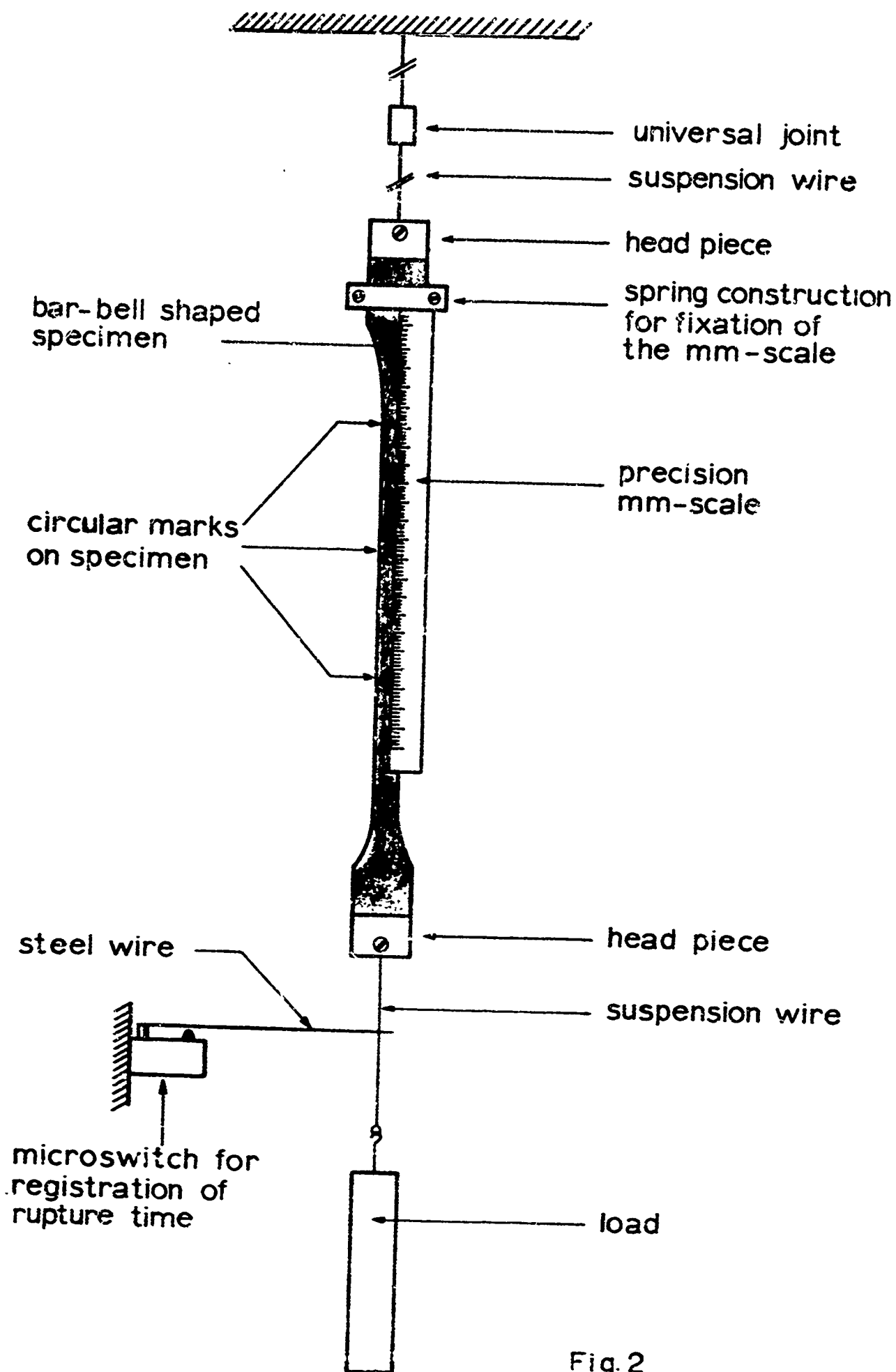


Fig. 2

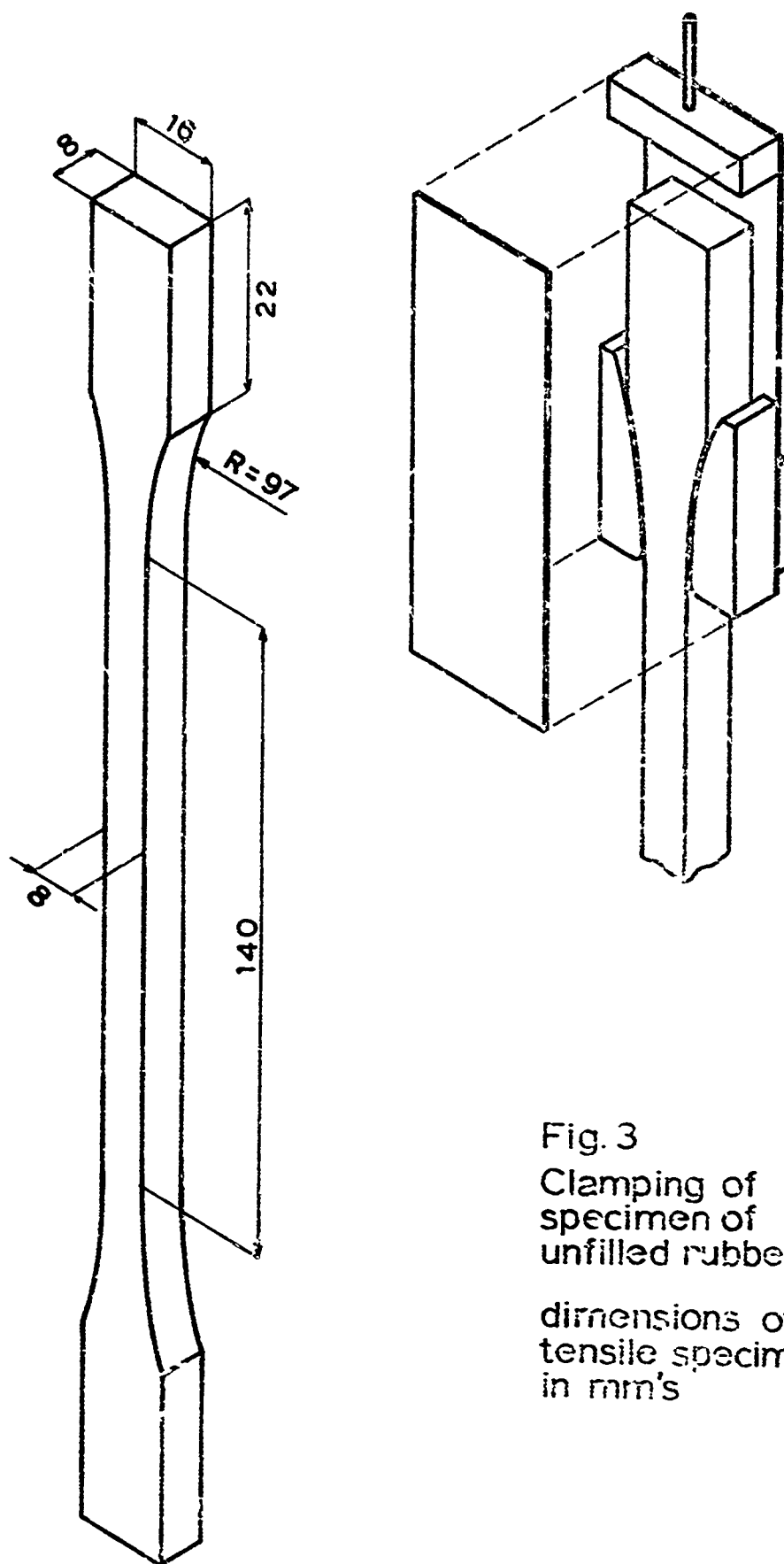


Fig. 3

Clamping of
specimen of
unfilled rubber

dimensions of
tensile specimen,
in mm's

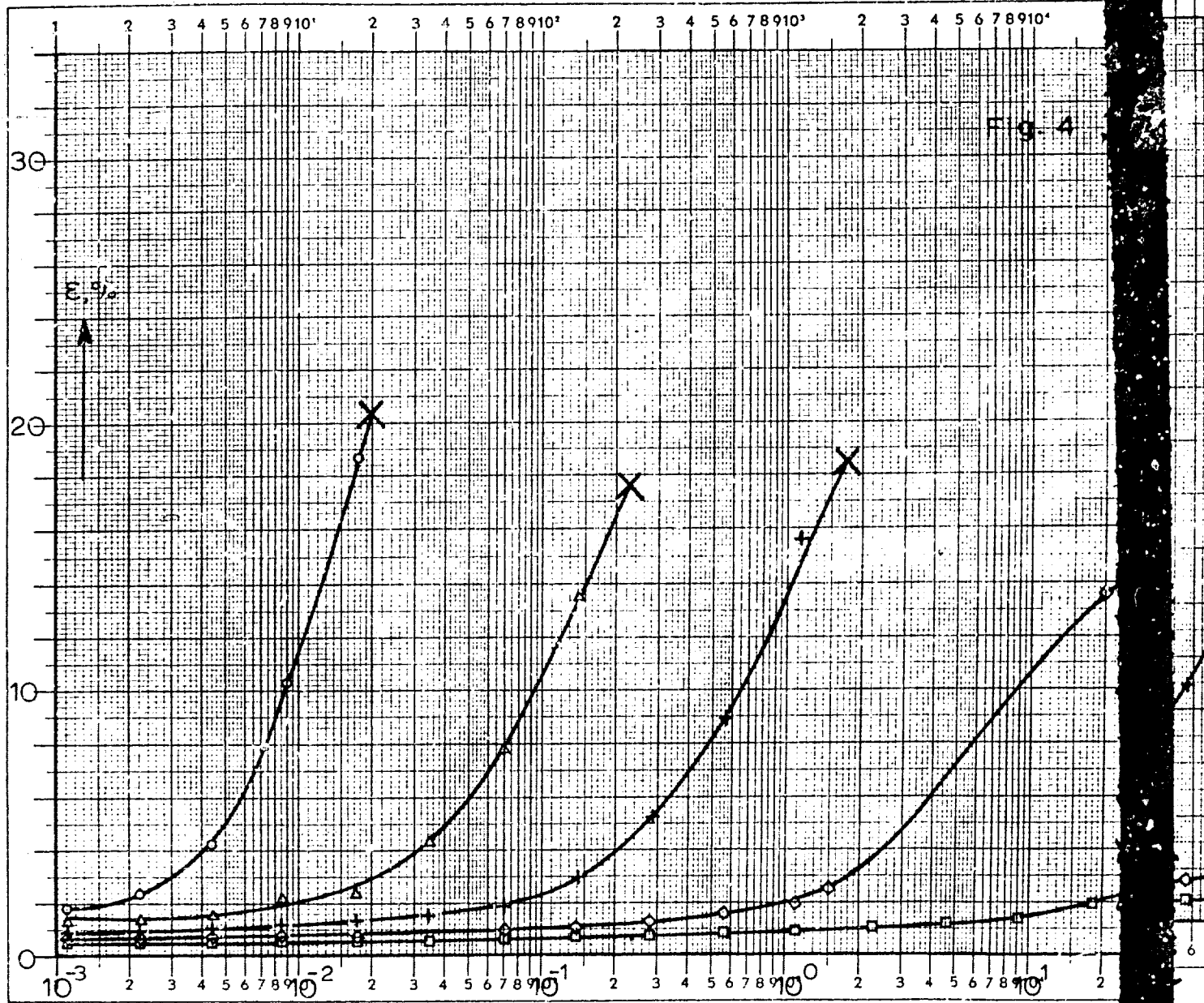
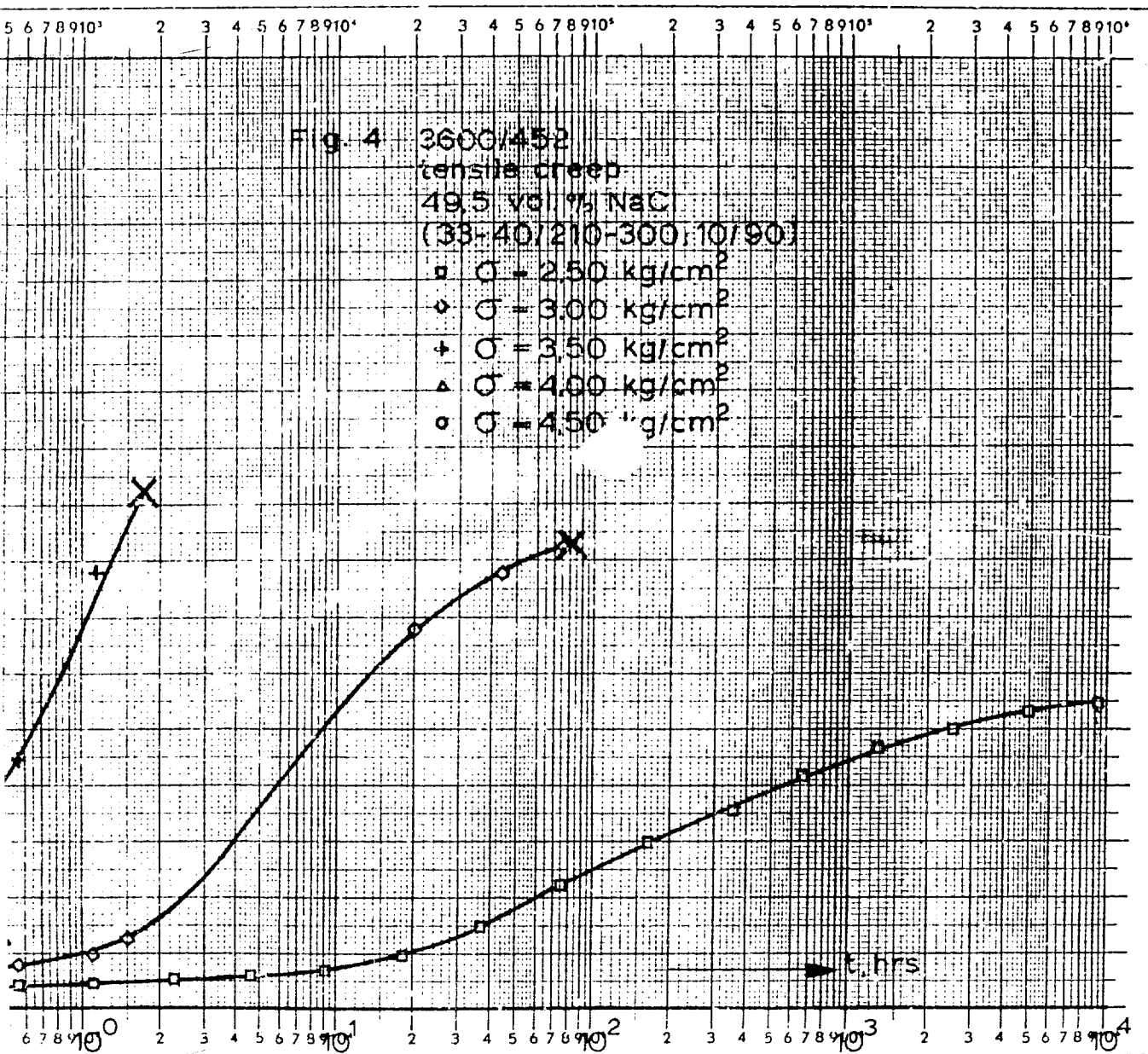


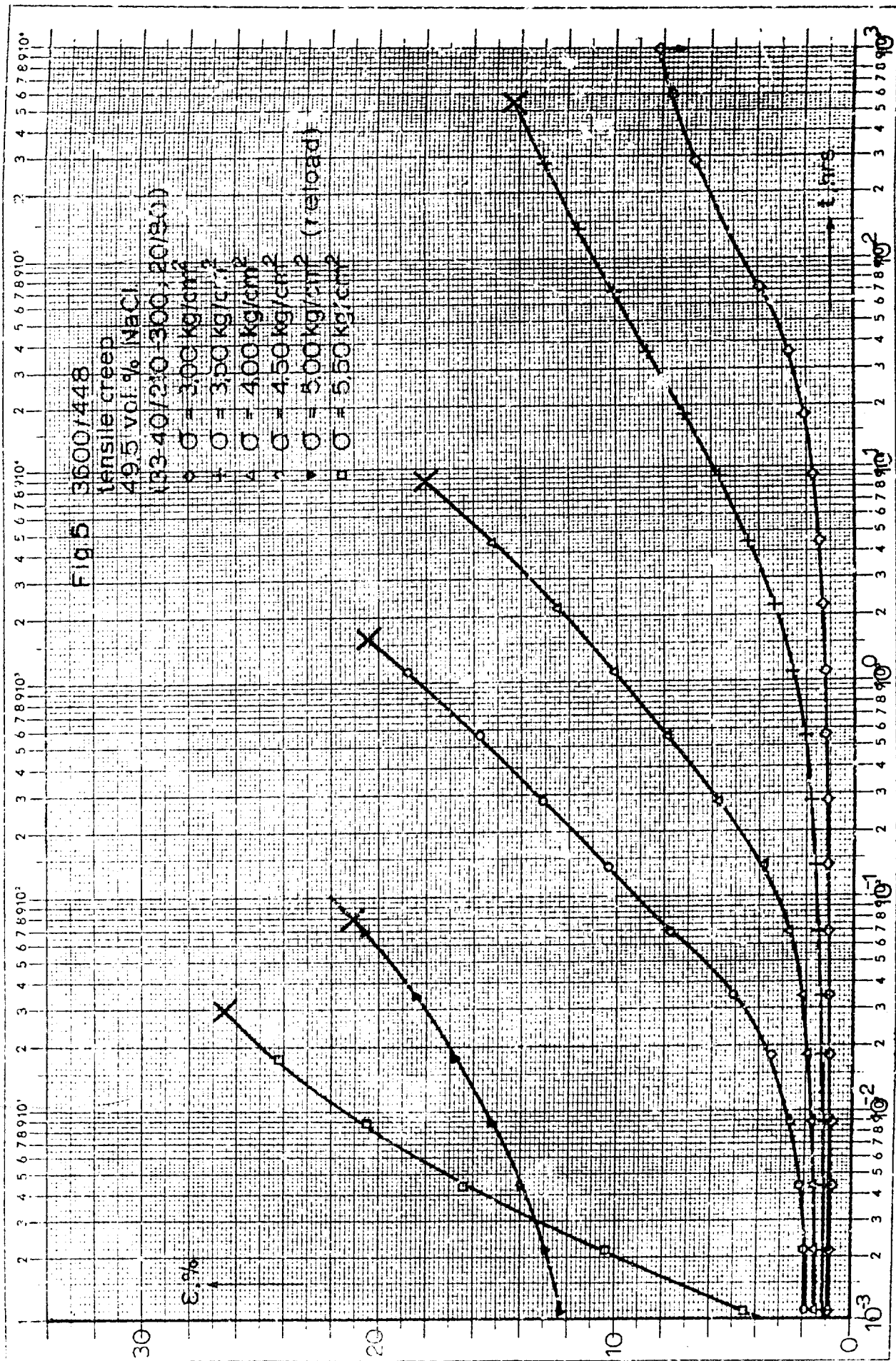
Fig. 4

A



No 34 X-as logar. verdeeld 1-10⁴ Eenheid 45 mm Y-as verdeeld 10⁴ Eenheid 45 mm. Y-as verdeeld in mm.

B



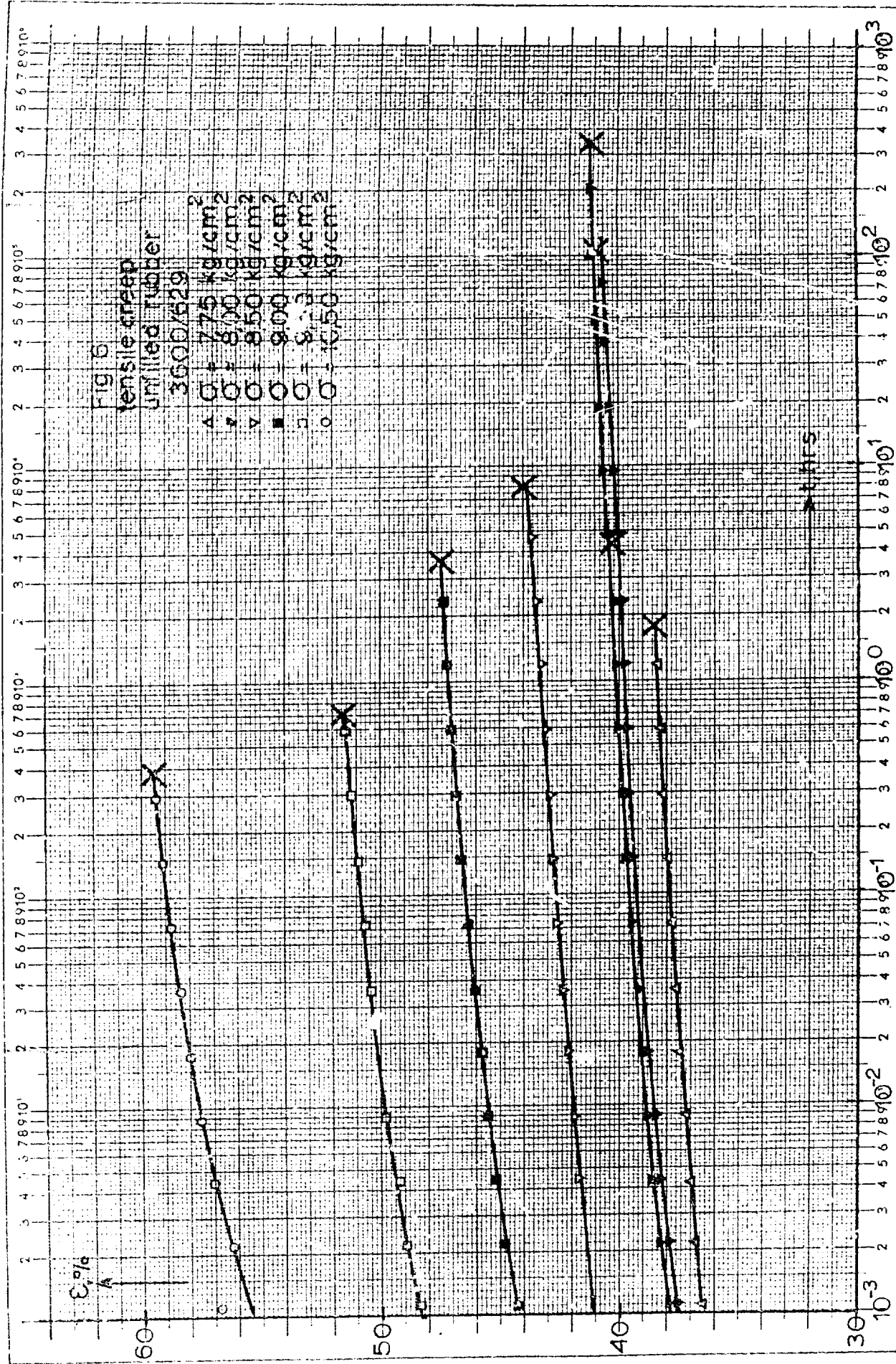
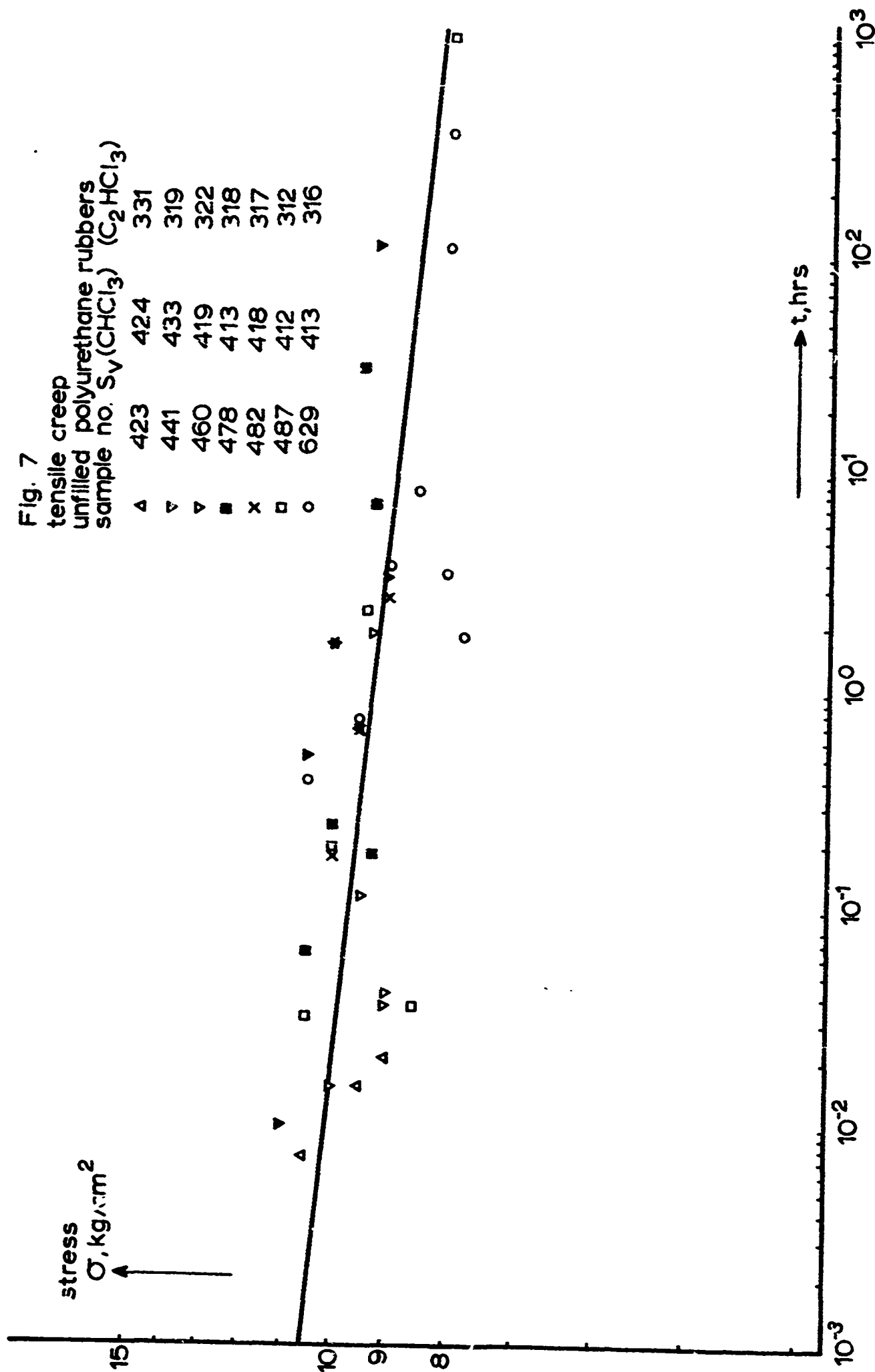


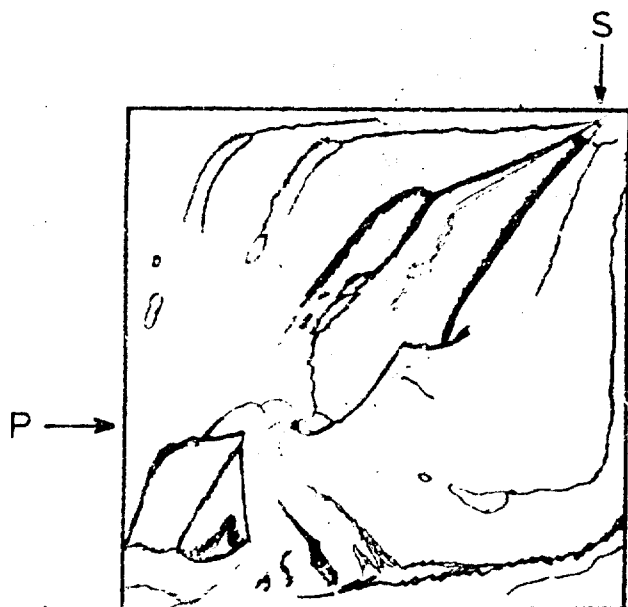
Fig. 7

tensile creep
unfilled polyurethane rubbers
sample no. $S_V(CHCl_3)$ (C_2HCl_3)

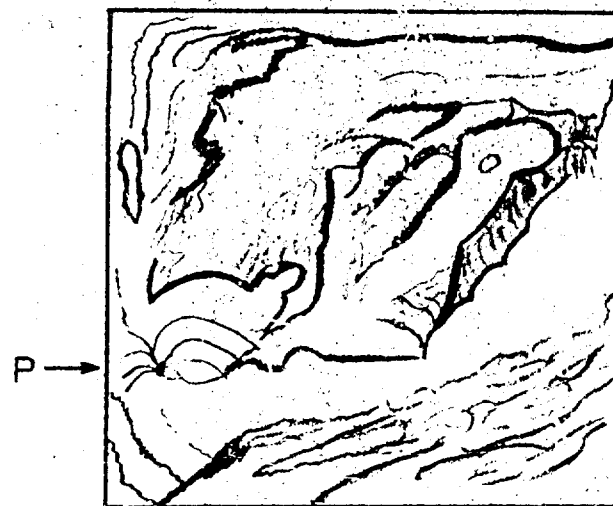
stress
 $\sigma, \text{kg/cm}^2$

$\rightarrow t, \text{hrs}$

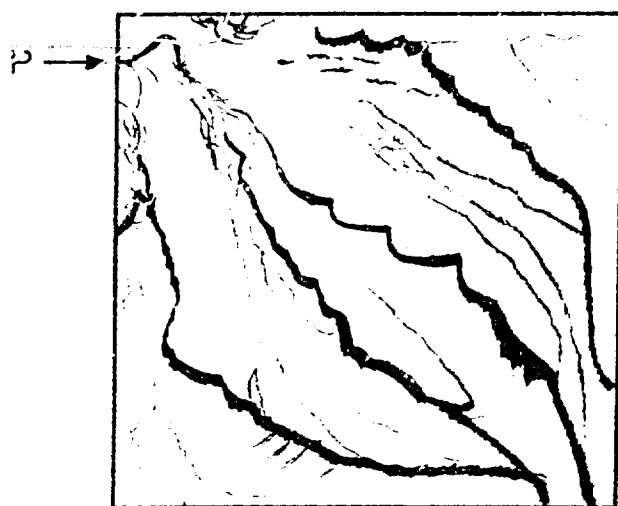




(a) specimen 629/5
 stress $8,5 \text{ kg/cm}^2$
 rupture time 7,9 hrs



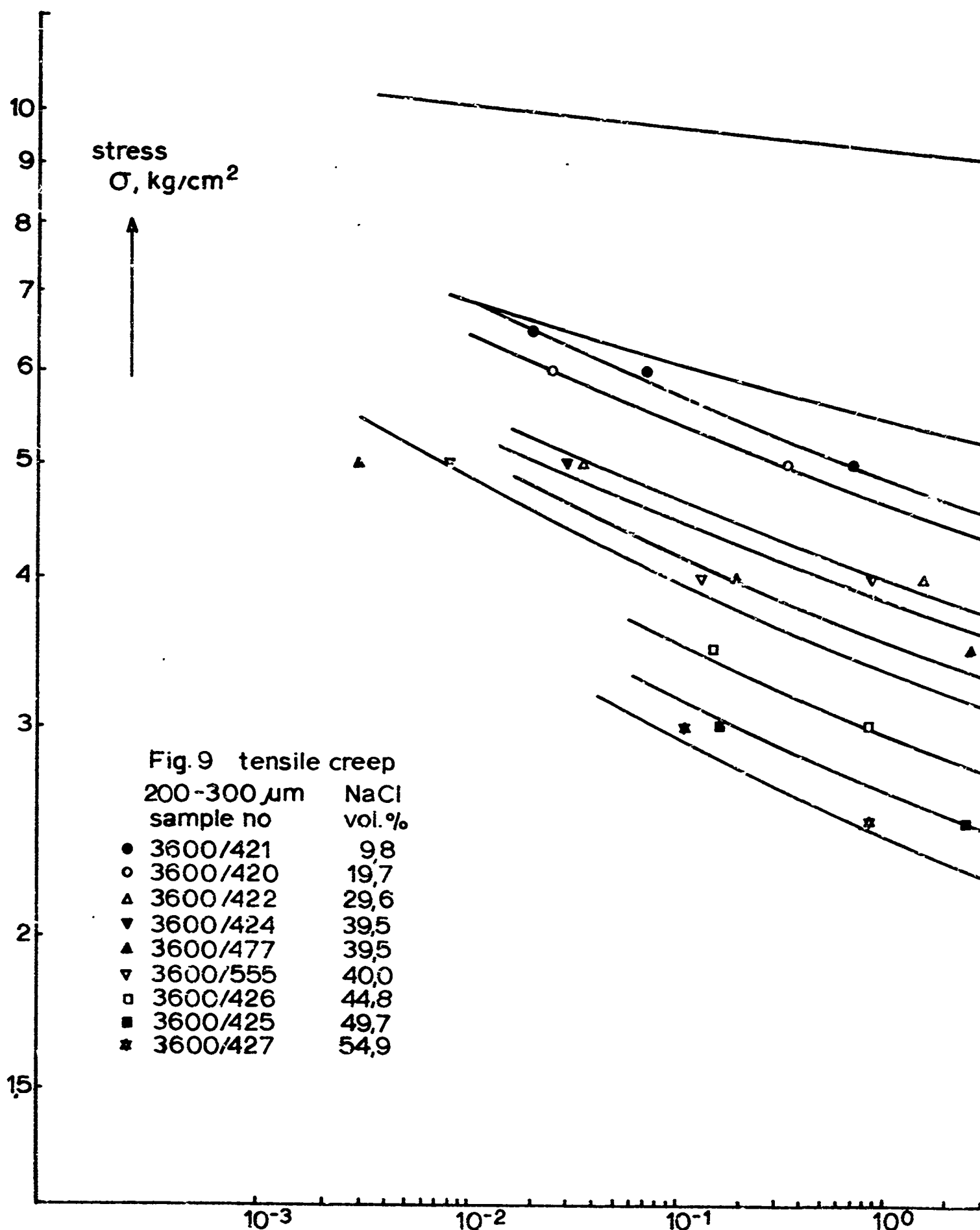
(b) specimen 629/2
 stress $7,75 \text{ kg/cm}^2$
 rupture time 1,75 hrs

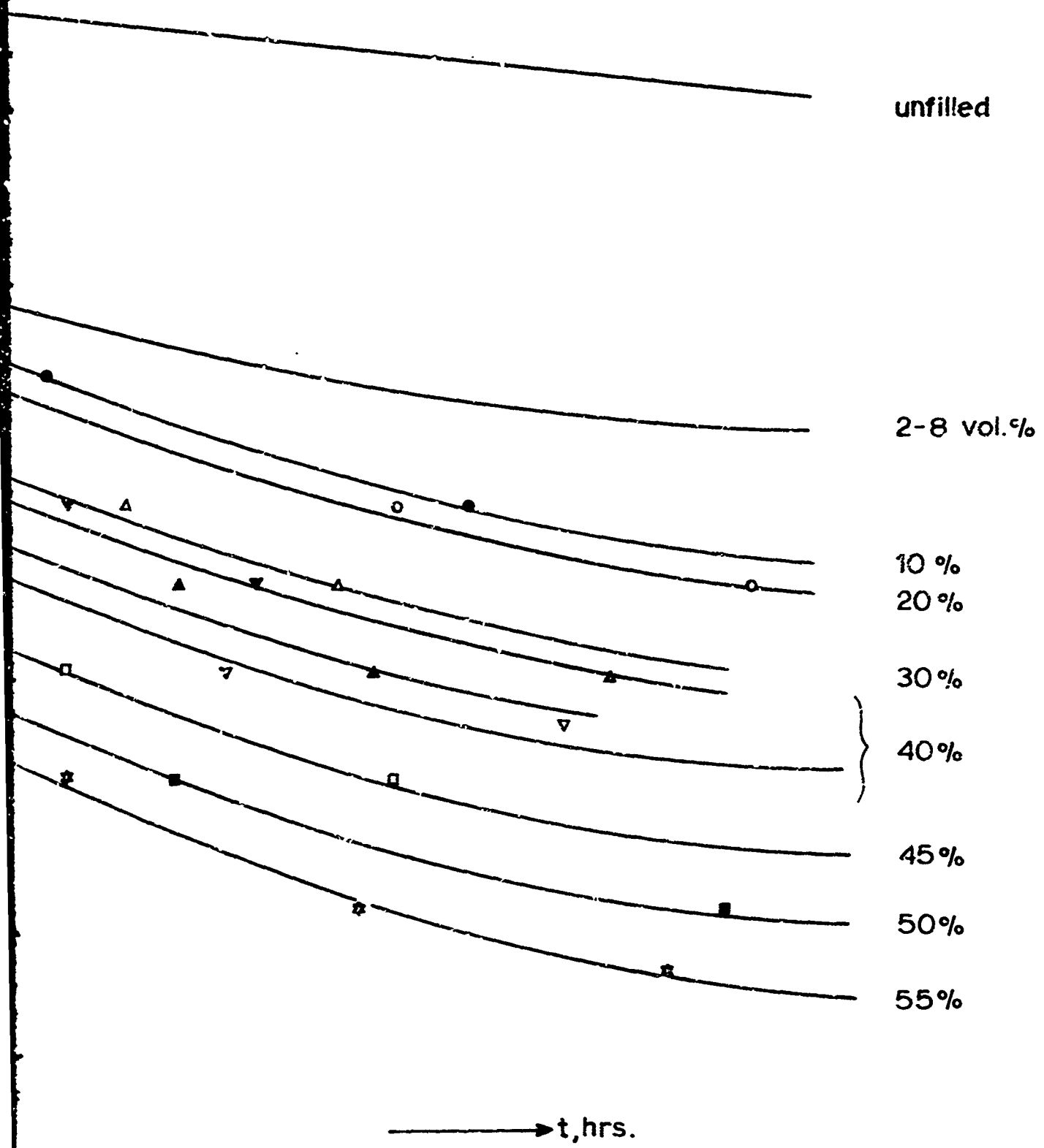


(c) specimen 629/6
 stress $10,5 \text{ kg/cm}^2$
 rupture time 0,38 hrs

Fig. 8 Fracture surfaces
 of unfilled rubber 3600/629

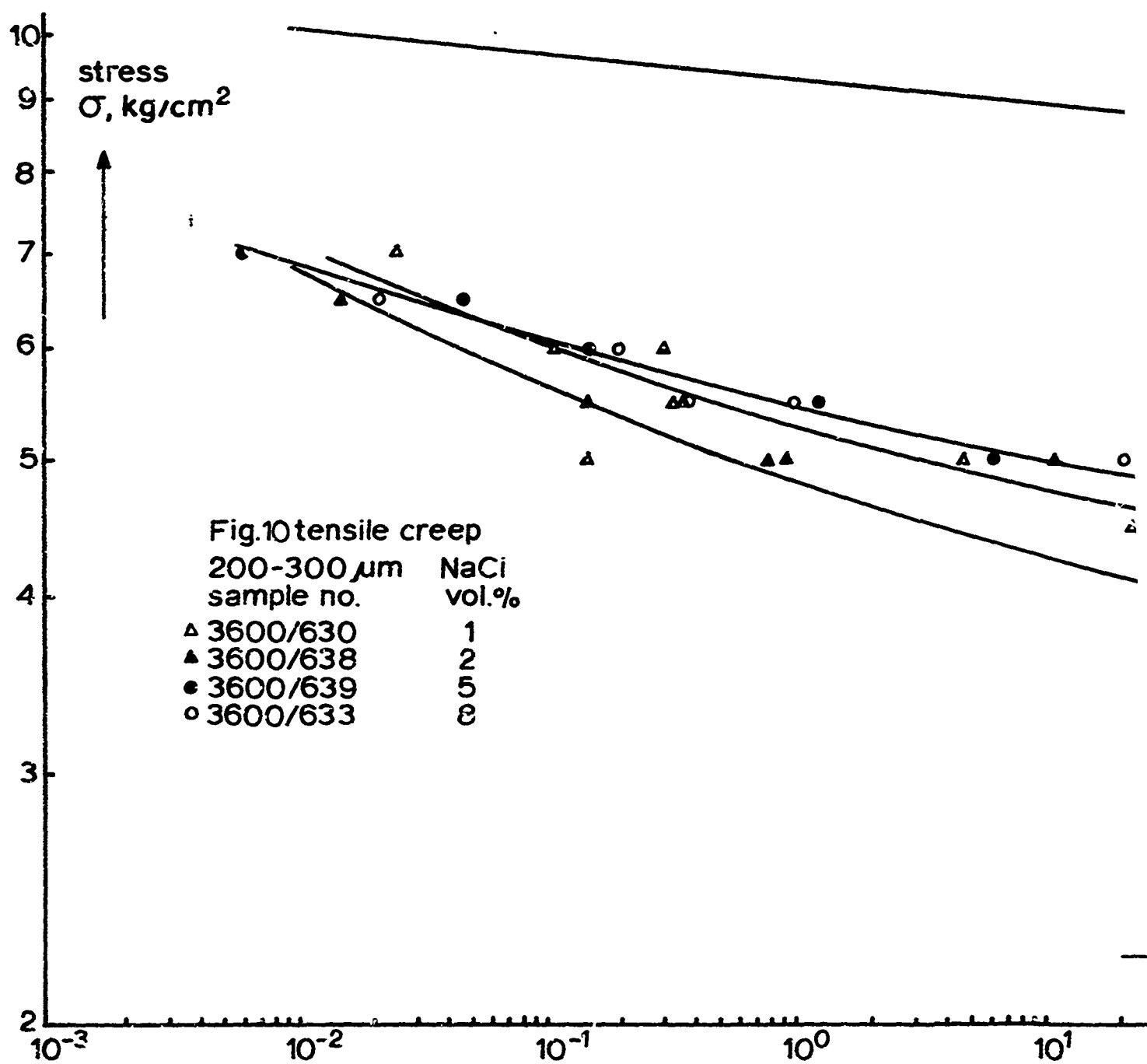
P = origin of primary fracture
 S = origin of secondary fracture



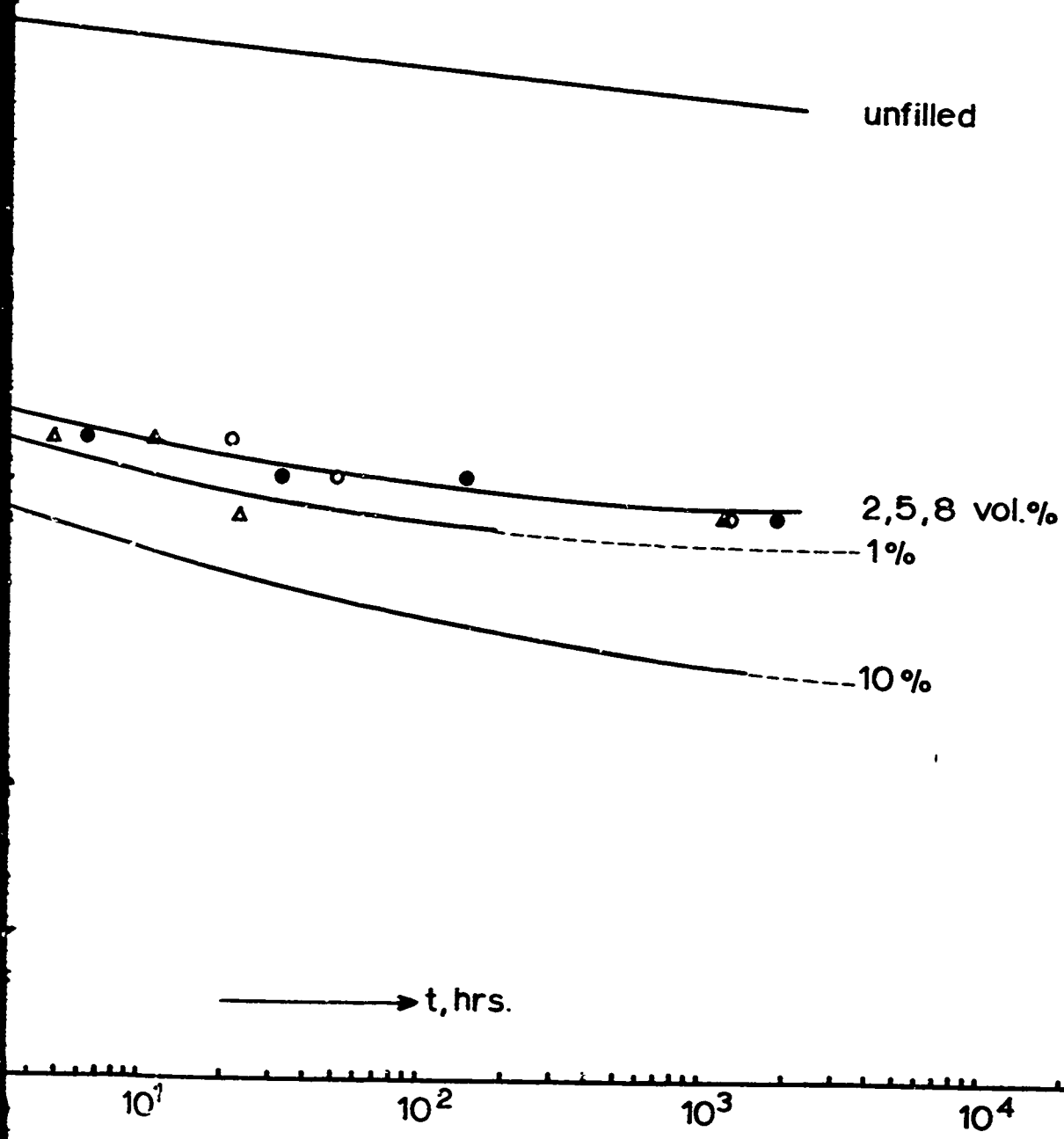


10⁰ 10¹ 10² 10³ 10⁴

B

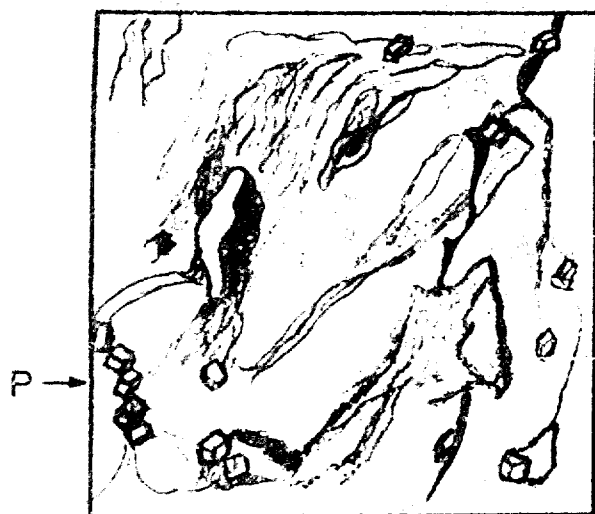


A

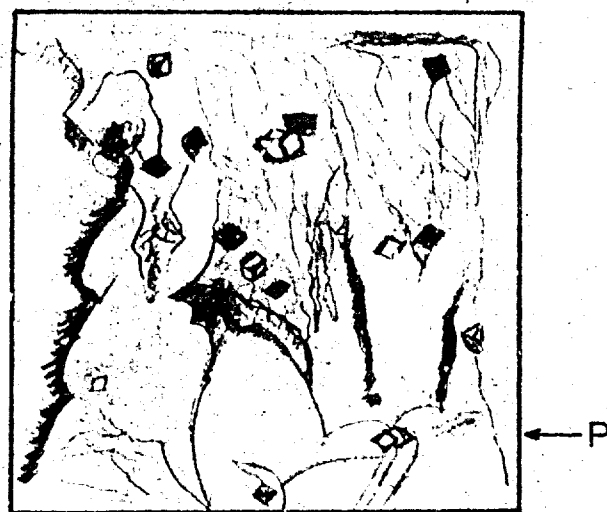


B

Fig.11 Fracture surfaces of rubbers filled with coarse sodium chloride



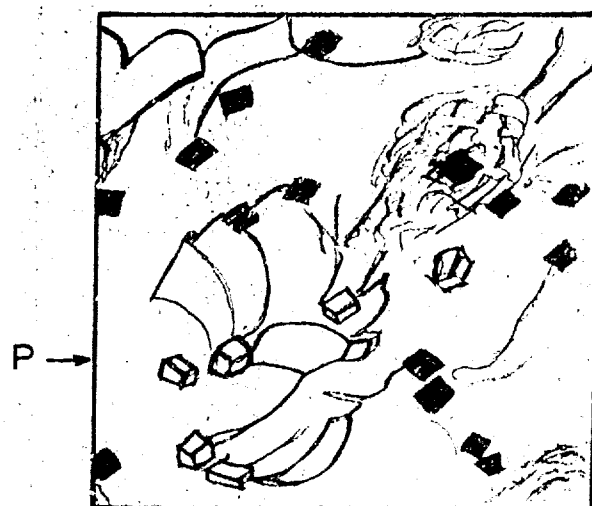
(a) specimen 630/6
stress 6.0 kg/cm^2
rupture time 0.11 hrs
 $c = 1 \text{ vol.}\%$



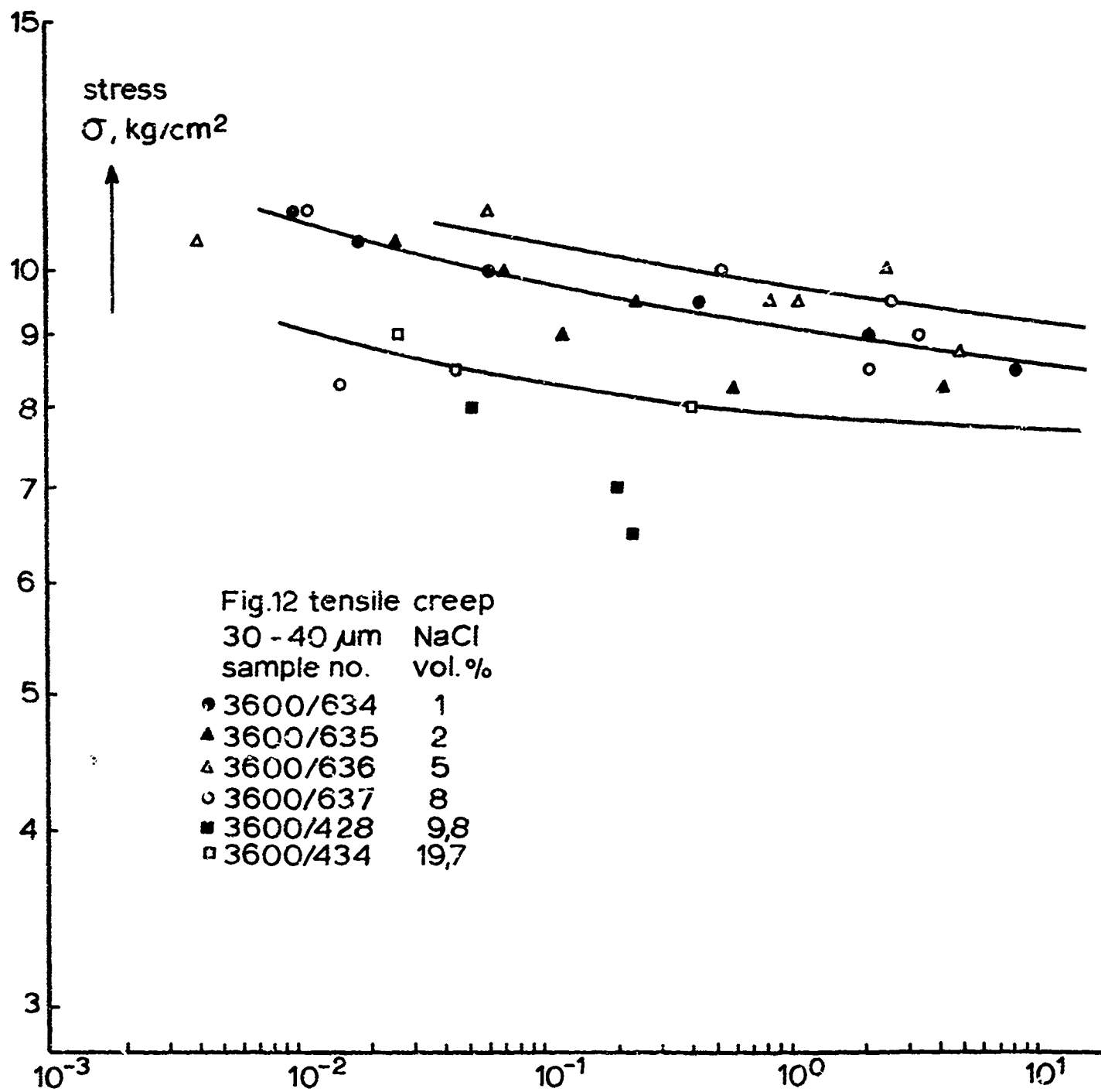
(b) specimen 630/7
stress 5.0 kg/cm^2
rupture time 4.8 hrs
 $c = 1 \text{ vol.}\%$



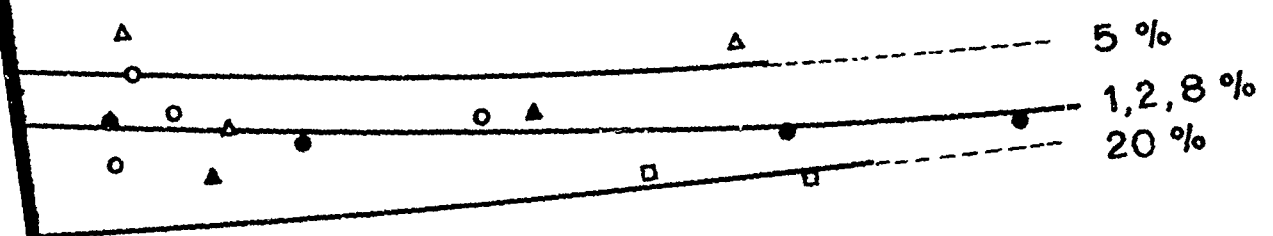
(c) specimen 638/8
stress 5.5 kg/cm^2
rupture time 0.36 hrs
 $c = 2 \text{ vol.}\%$



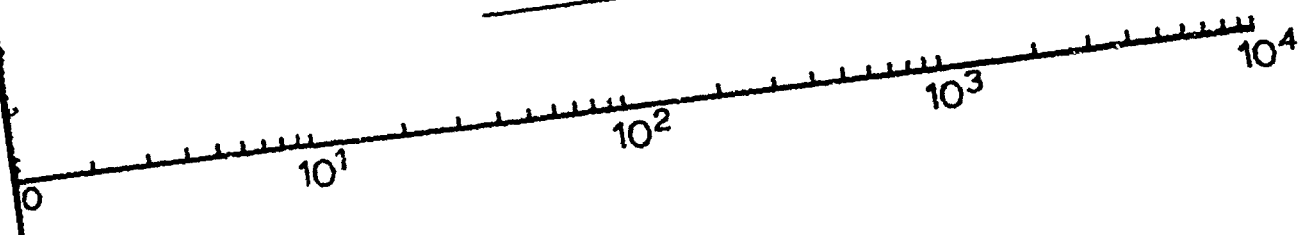
(d) specimen 633/2
stress 6.0 kg/cm^2
rupture time 0.2 hrs
 $c = 8 \text{ vol.}\%$
enlarged section of the
fracture surface



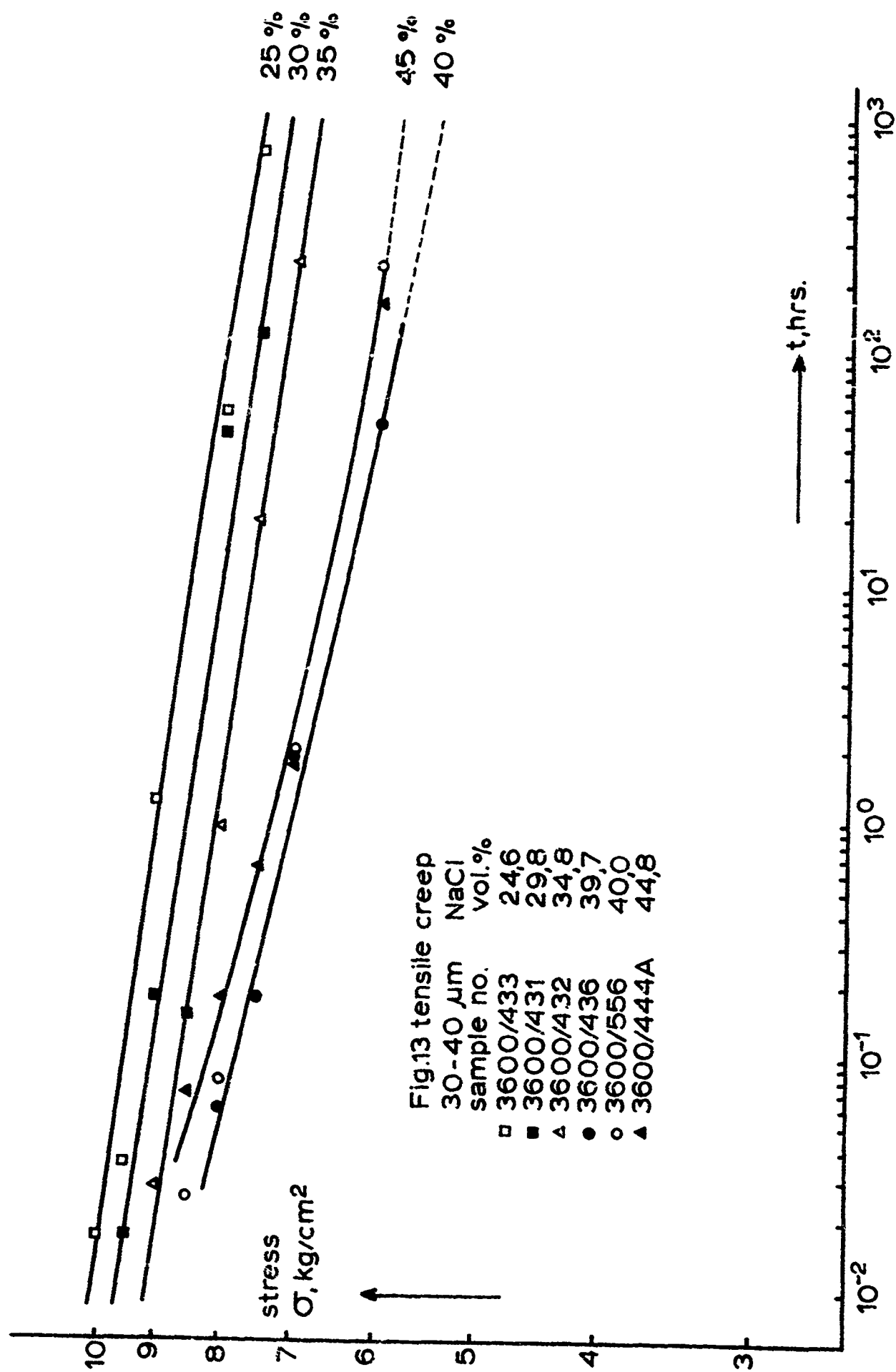
A

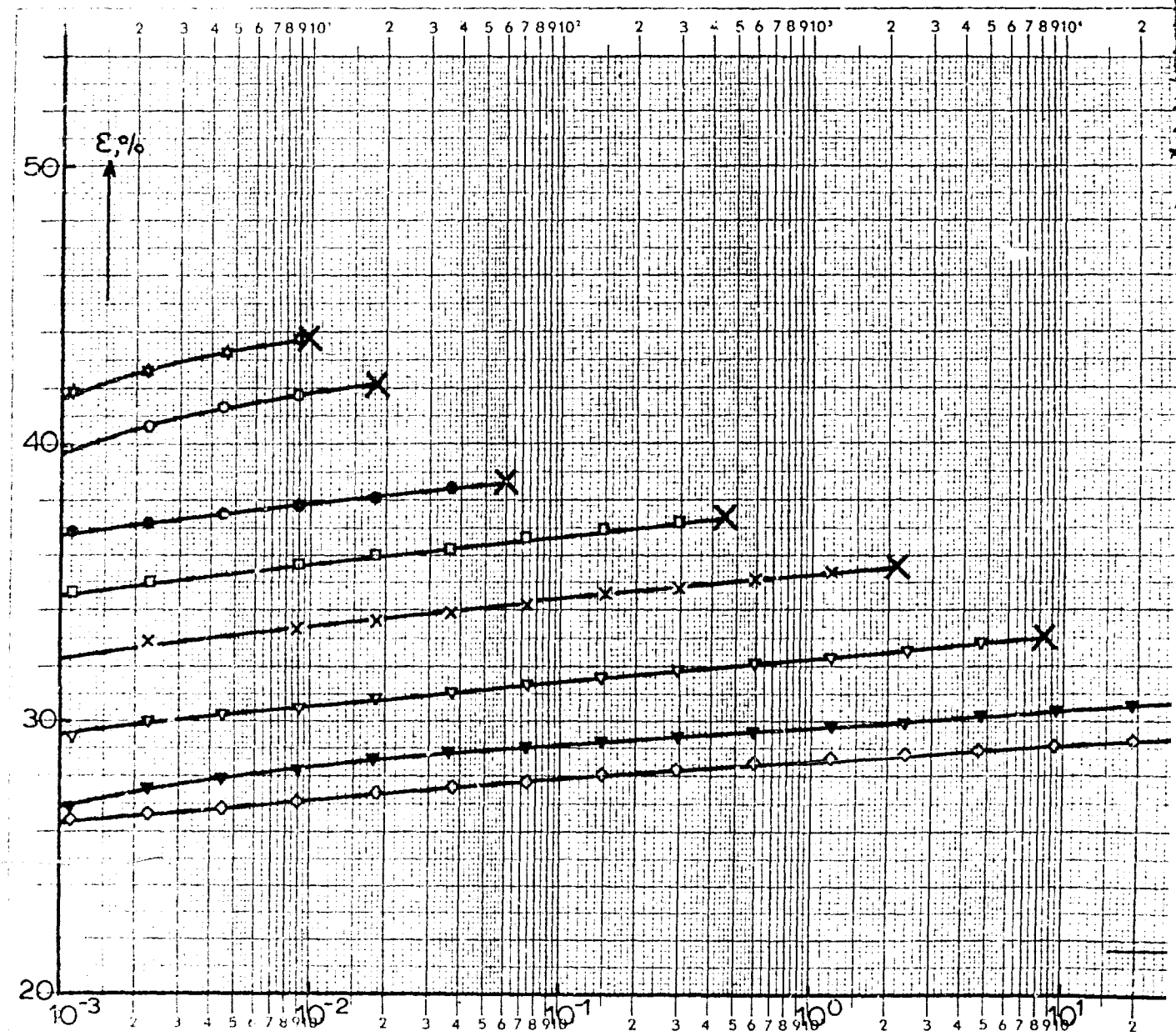


→ t, hrs.



B



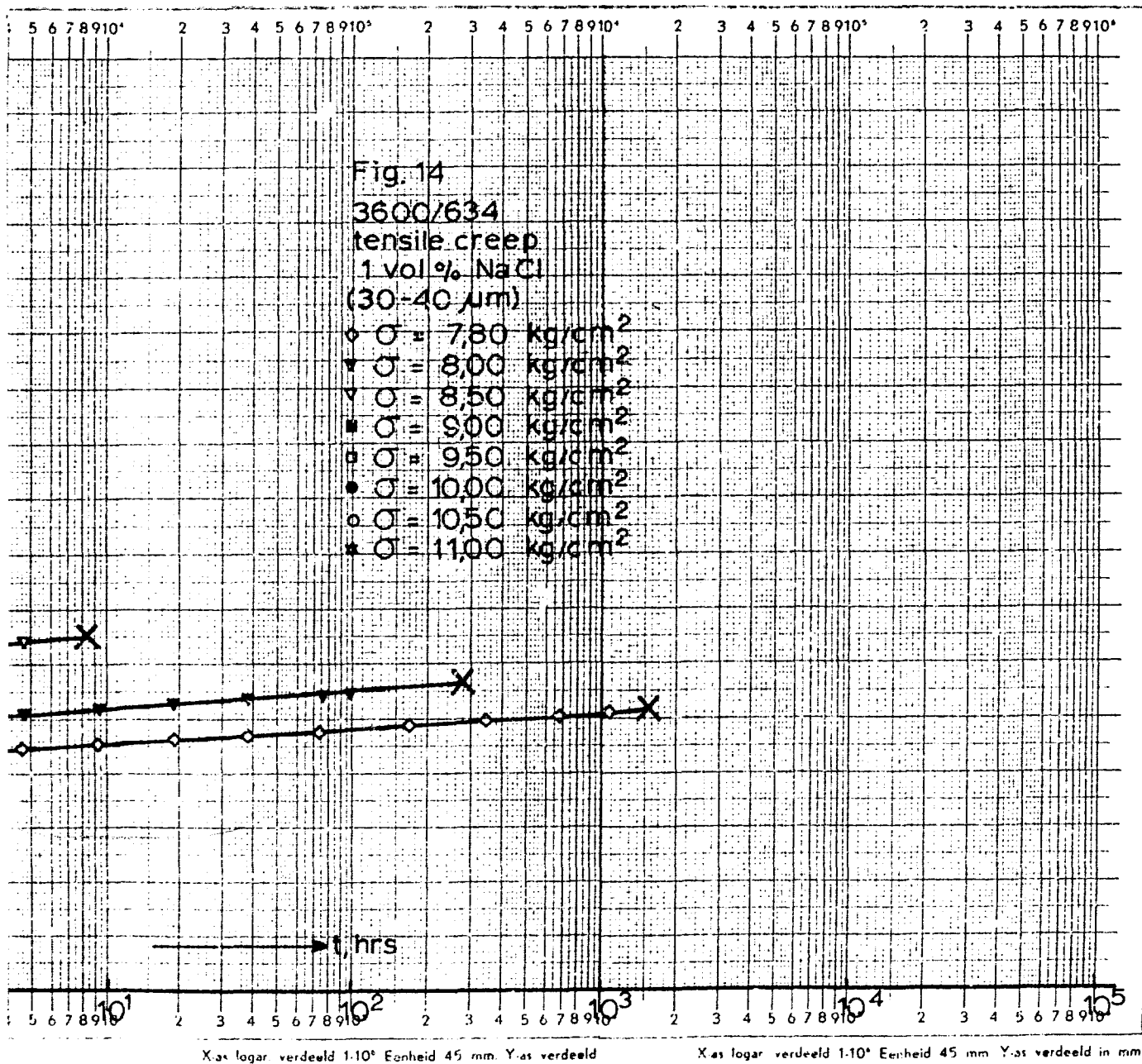


N.V. Dijkster, 'Mercurius' Wormerveer

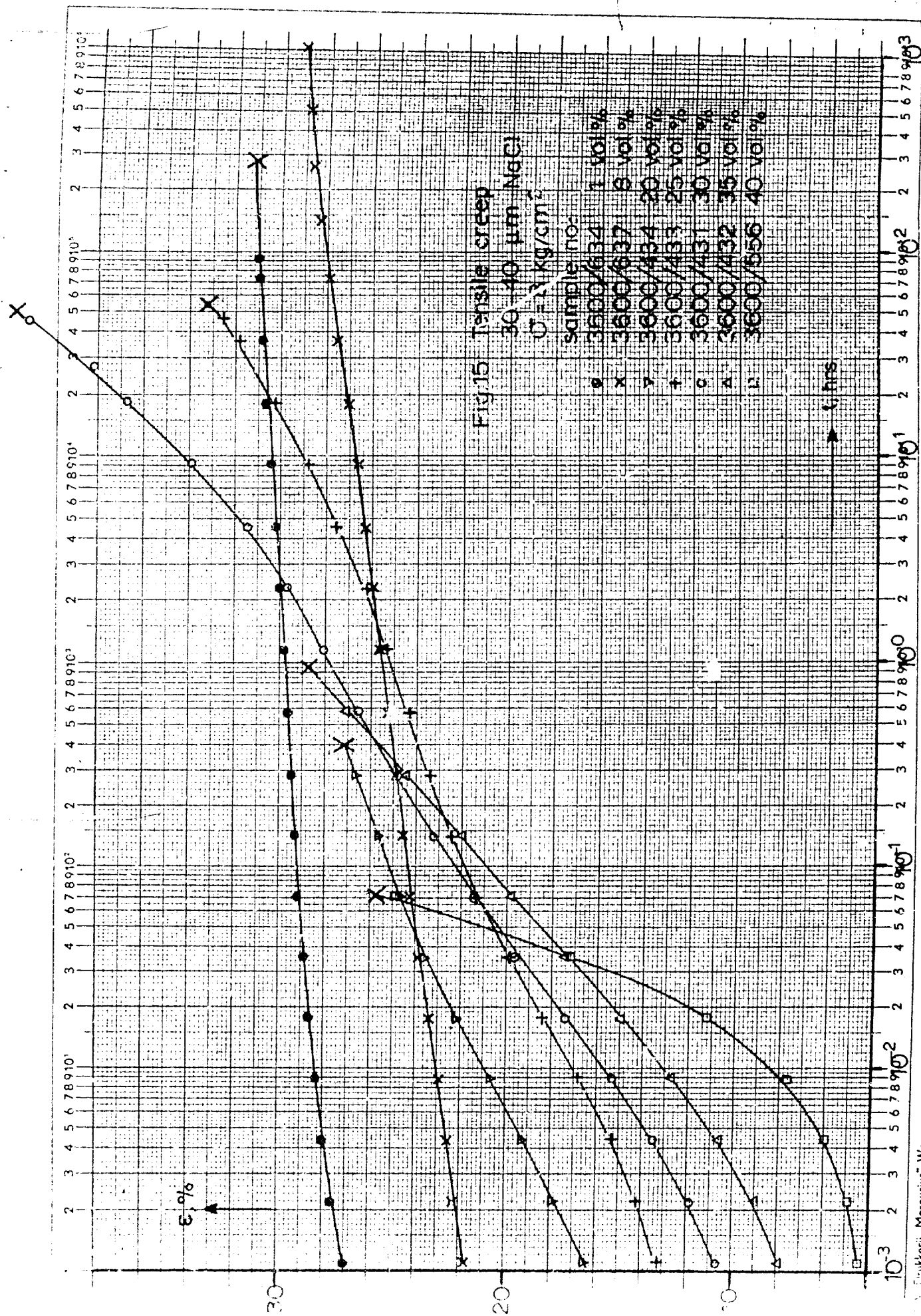
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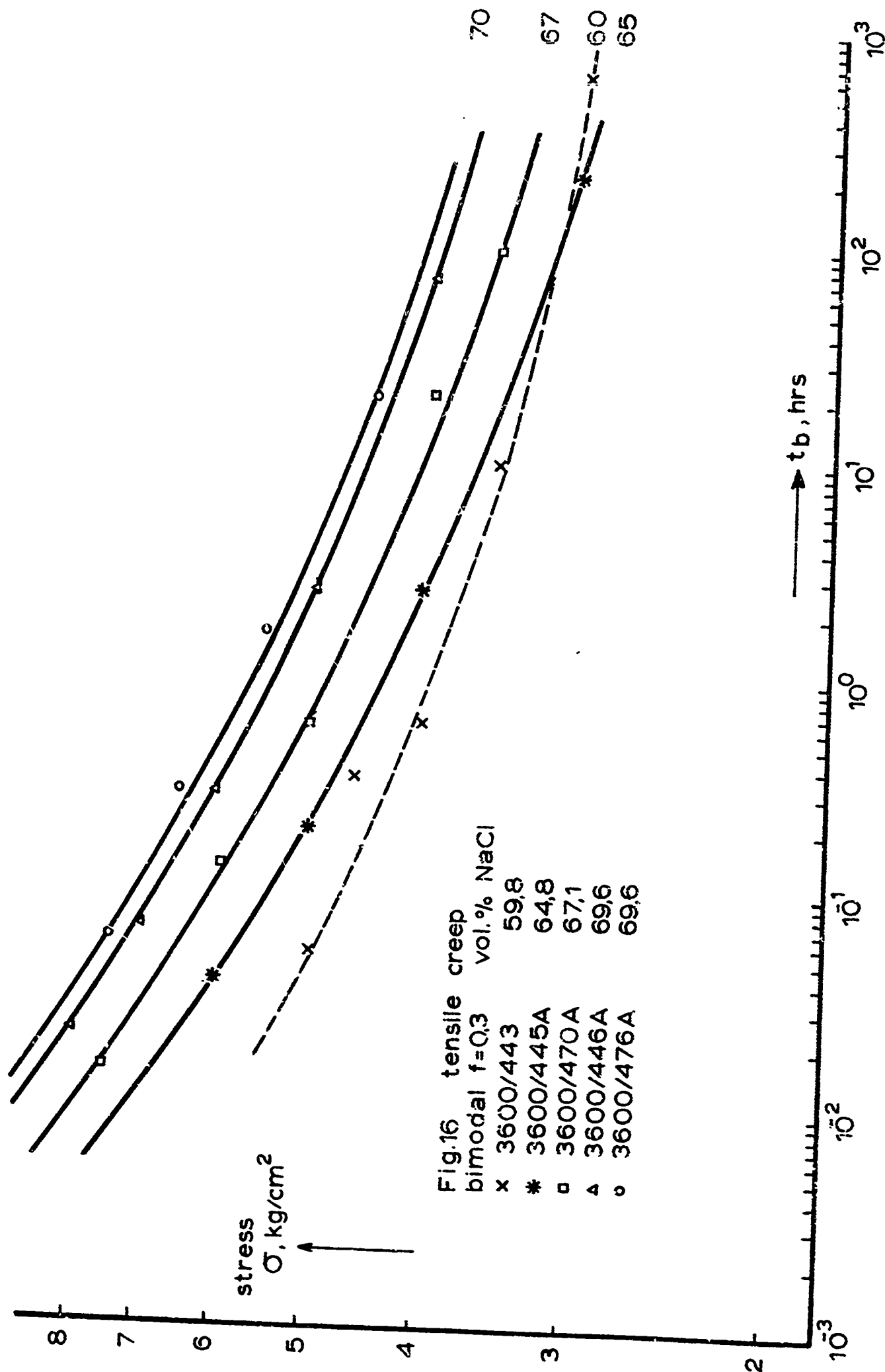
X

A



13





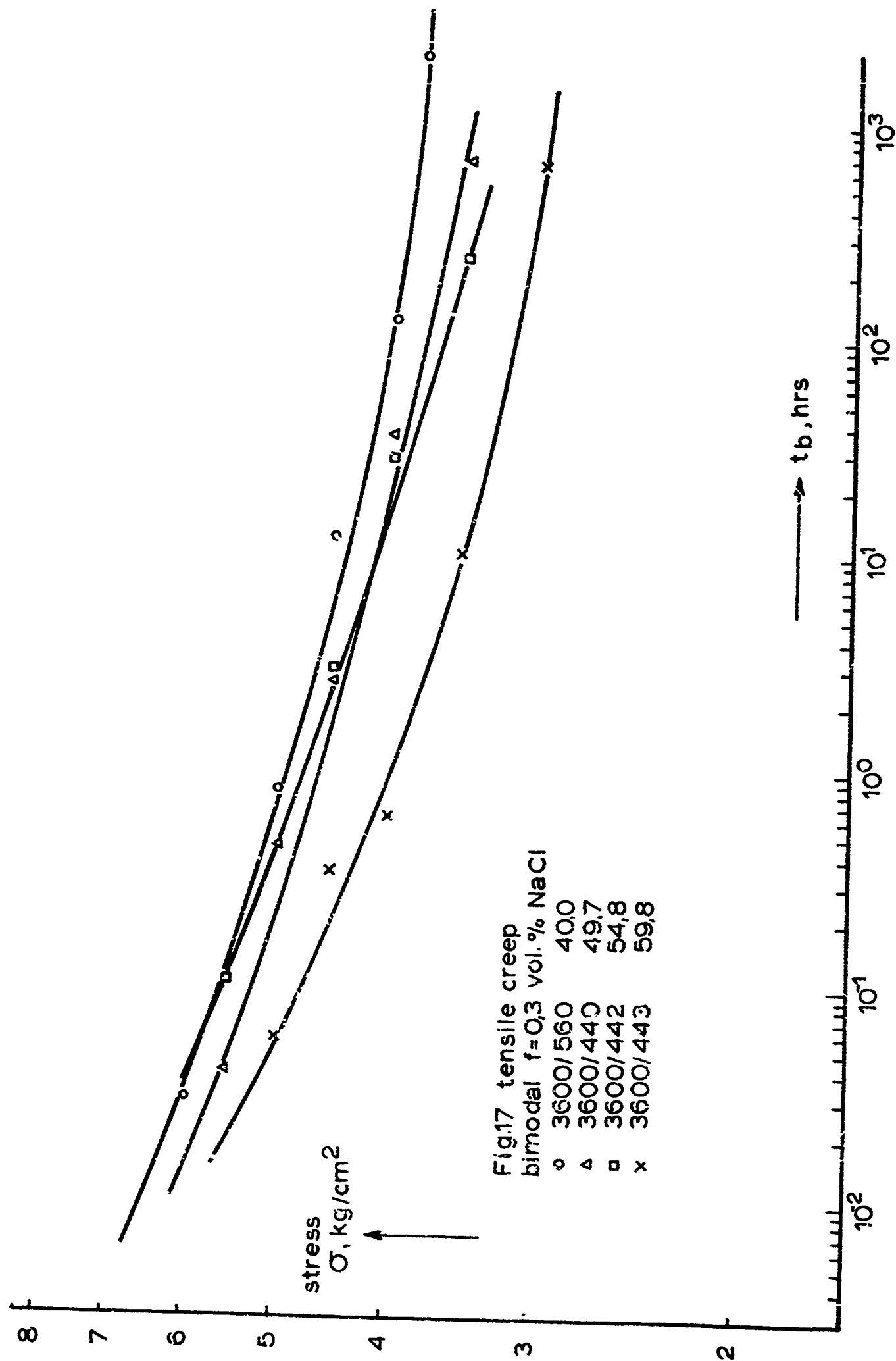
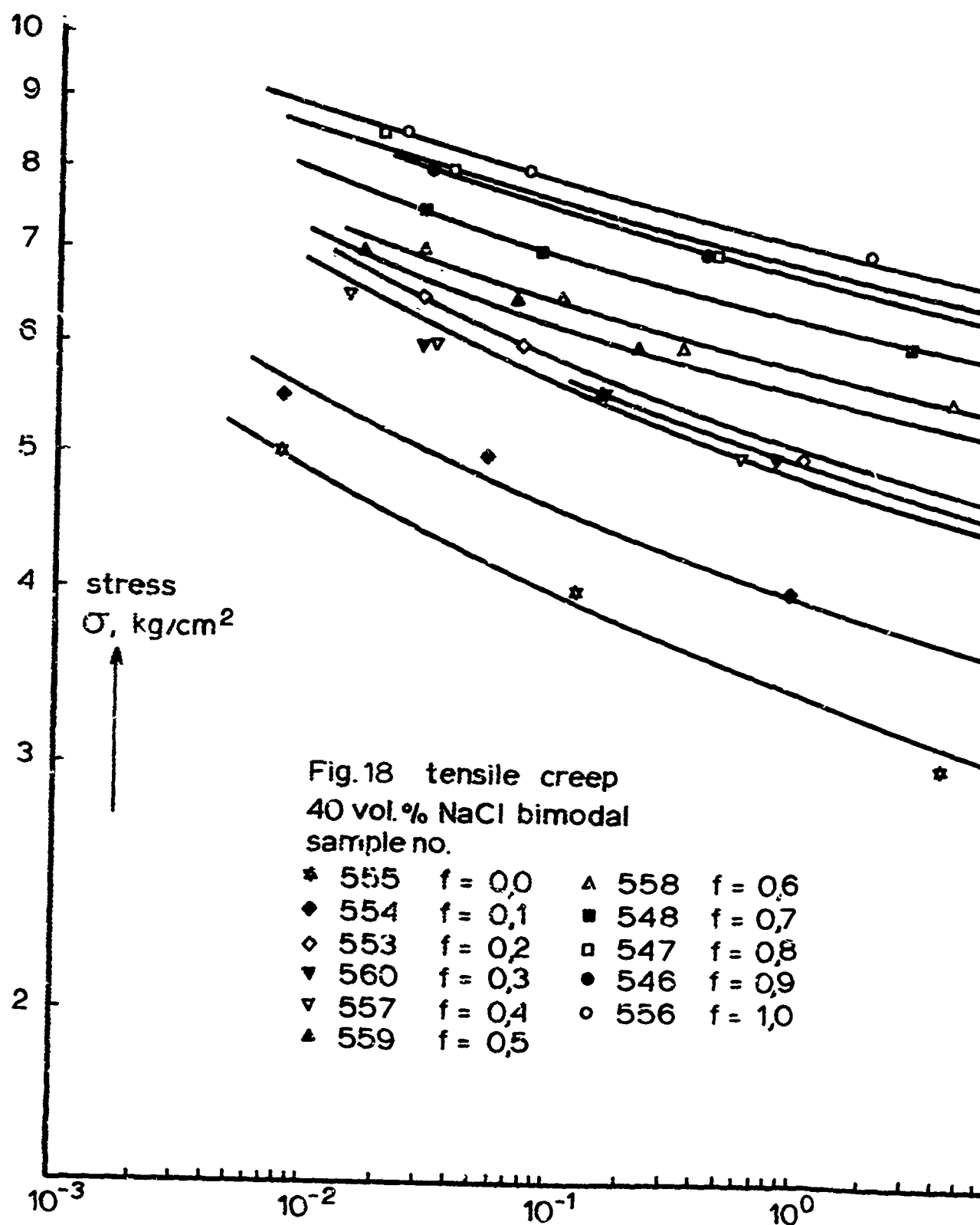
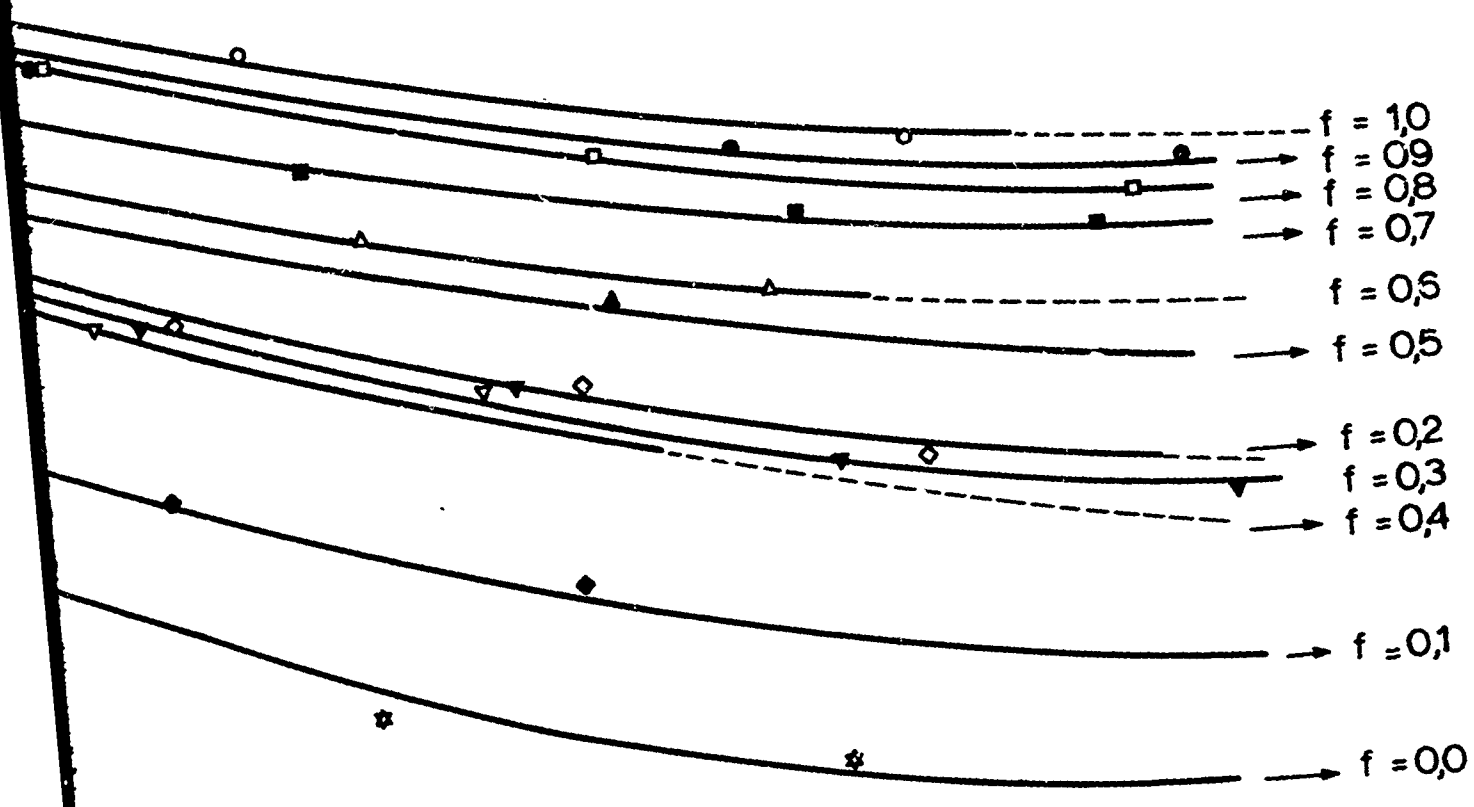


Fig17 tensile creep
bimodal $f=0,3$ vol. % NaCl



A



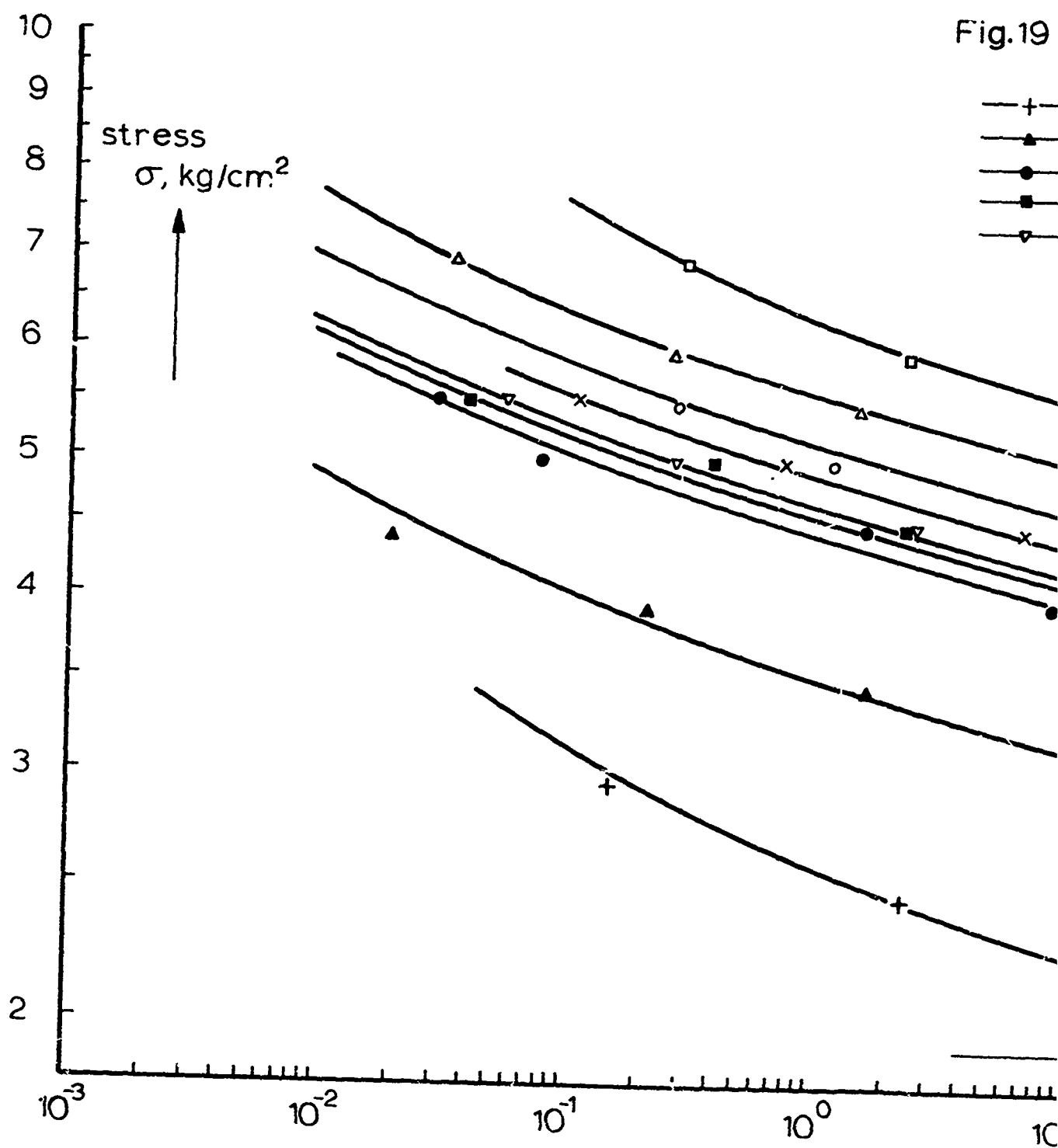
$f = 0,6$
 $f = 0,7$
 $f = 0,8$
 $f = 0,9$
 $f = 1,0$

→ t, hrs.

10^0 10^1 10^2 10^3 10^4

B

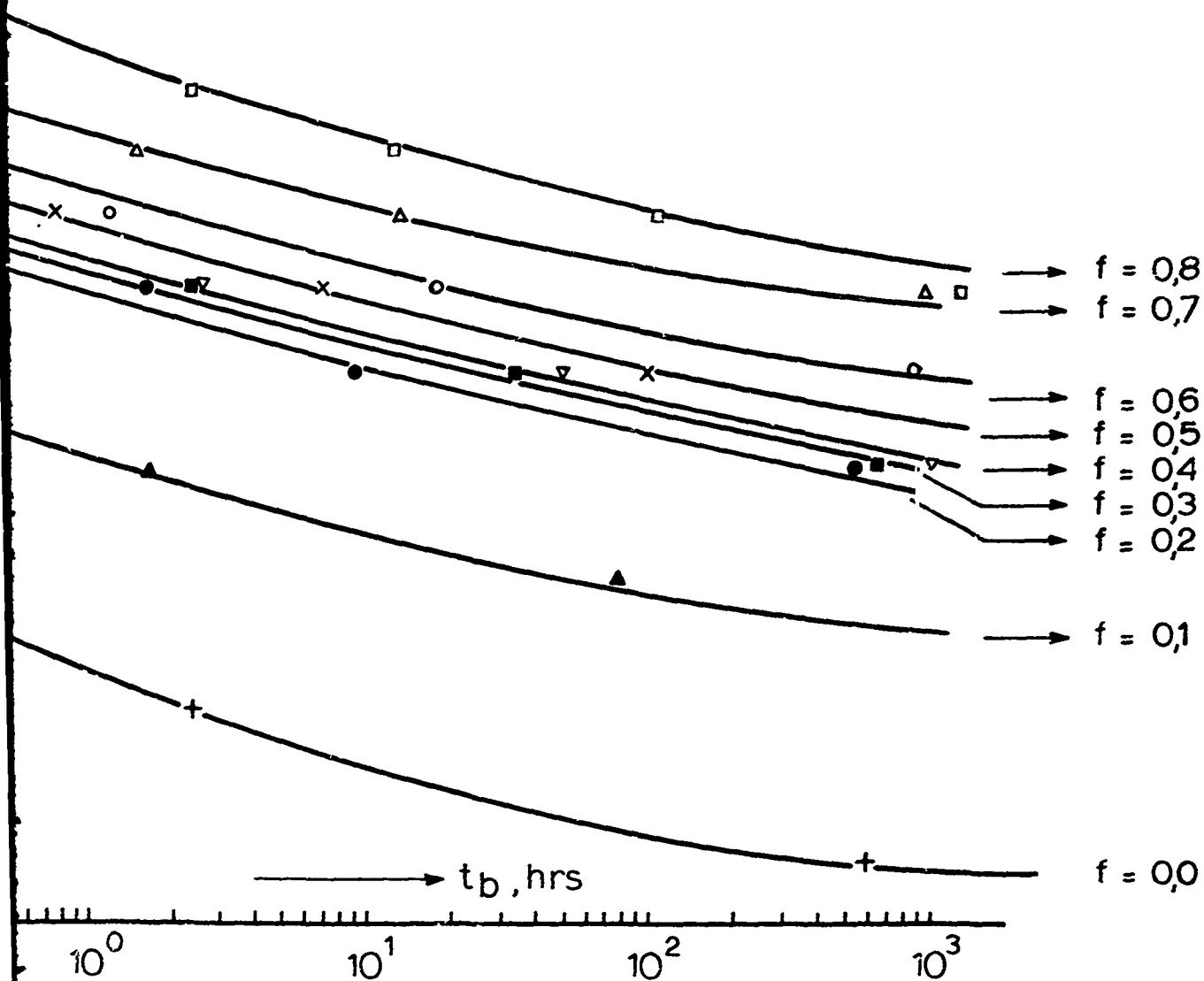
Fig.19



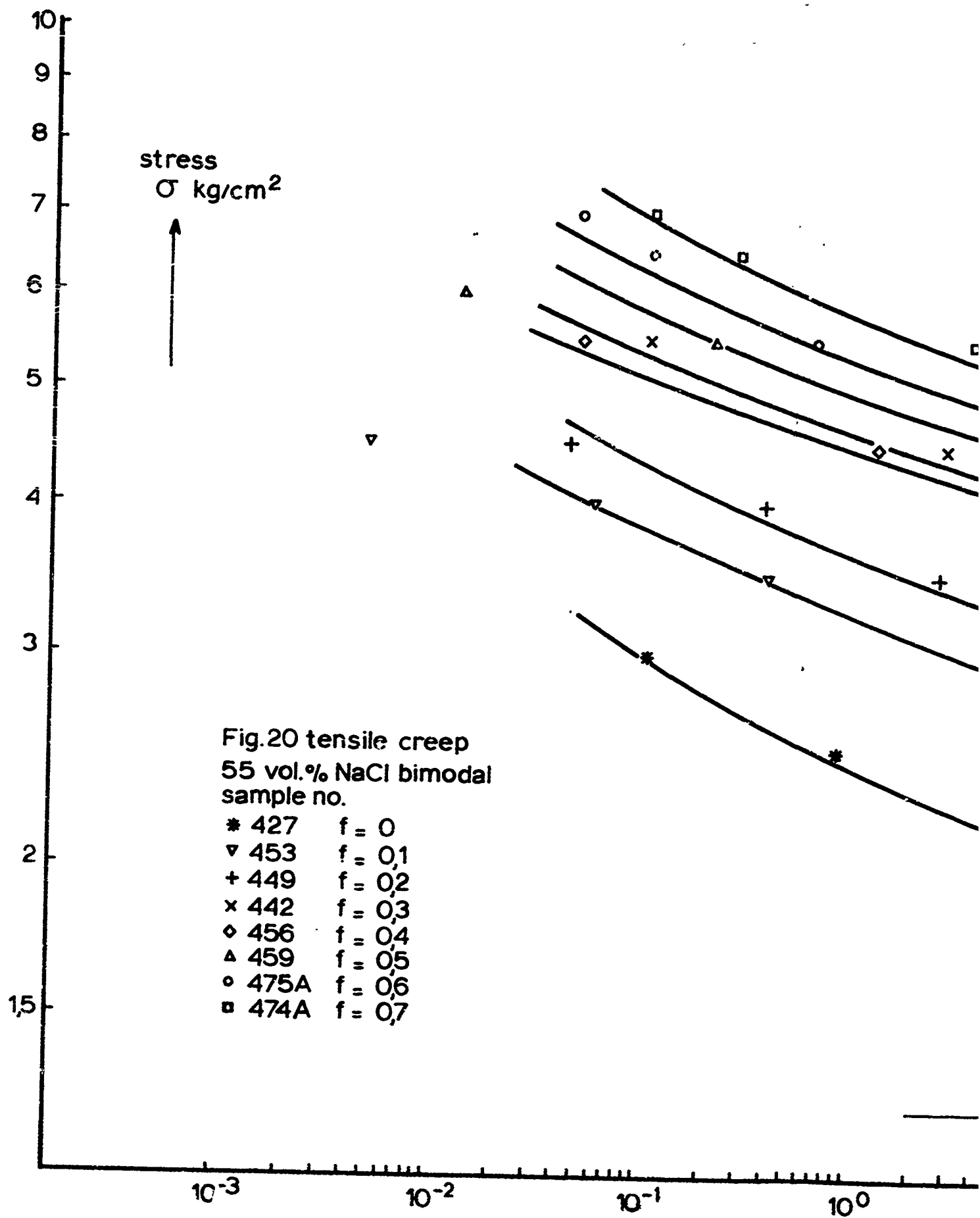
A

Fig.19 tensile creep
50 vol.% bimodal

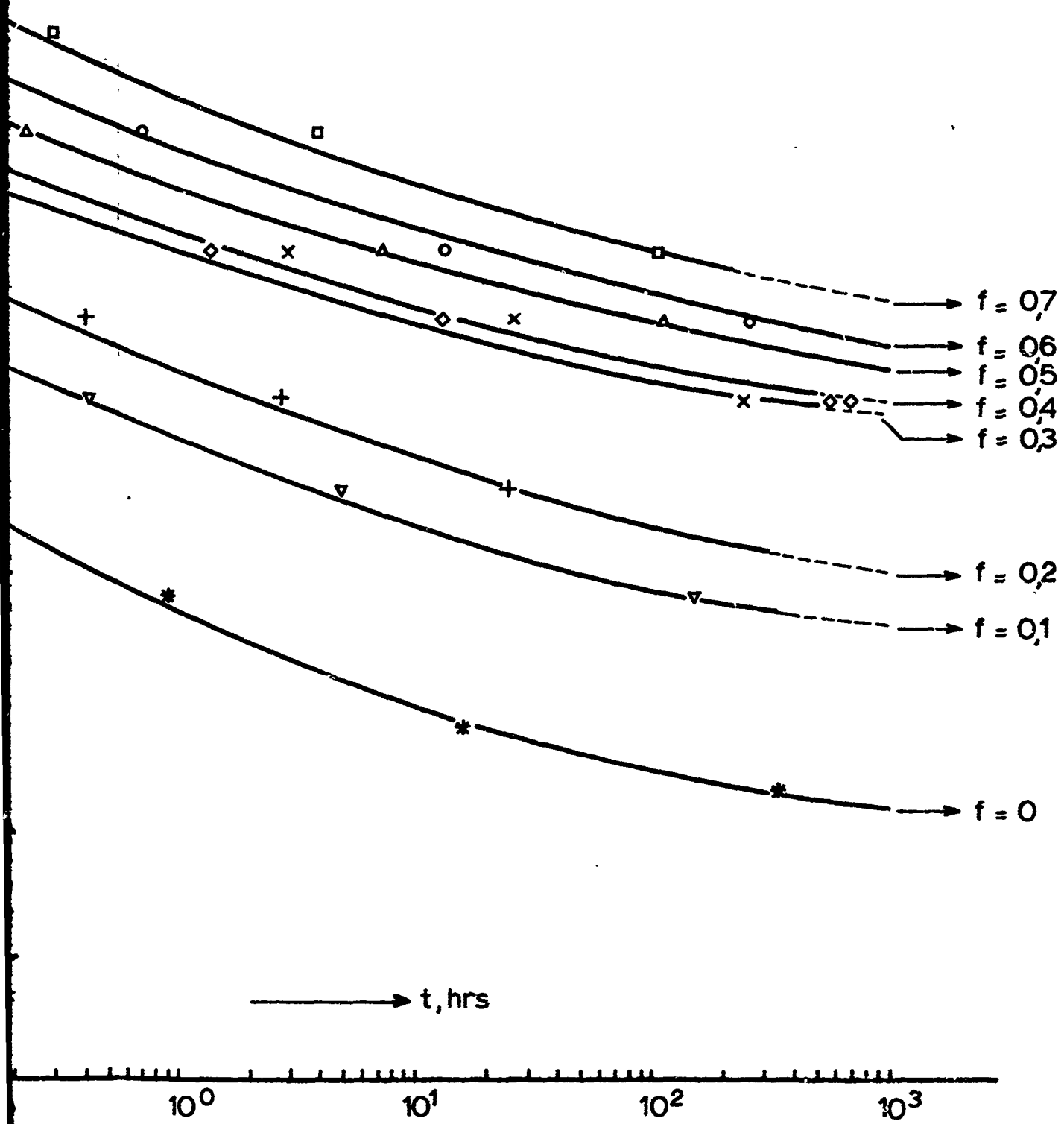
—+— $f=0.0$	—x— $f=0.5$
—▲— $f=0.1$	—○— $f=0.6$
—●— $f=0.2$	—△— $f=0.7$
—■— $f=0.3$	—□— $f=0.8$
—▽— $f=0.4$	



B

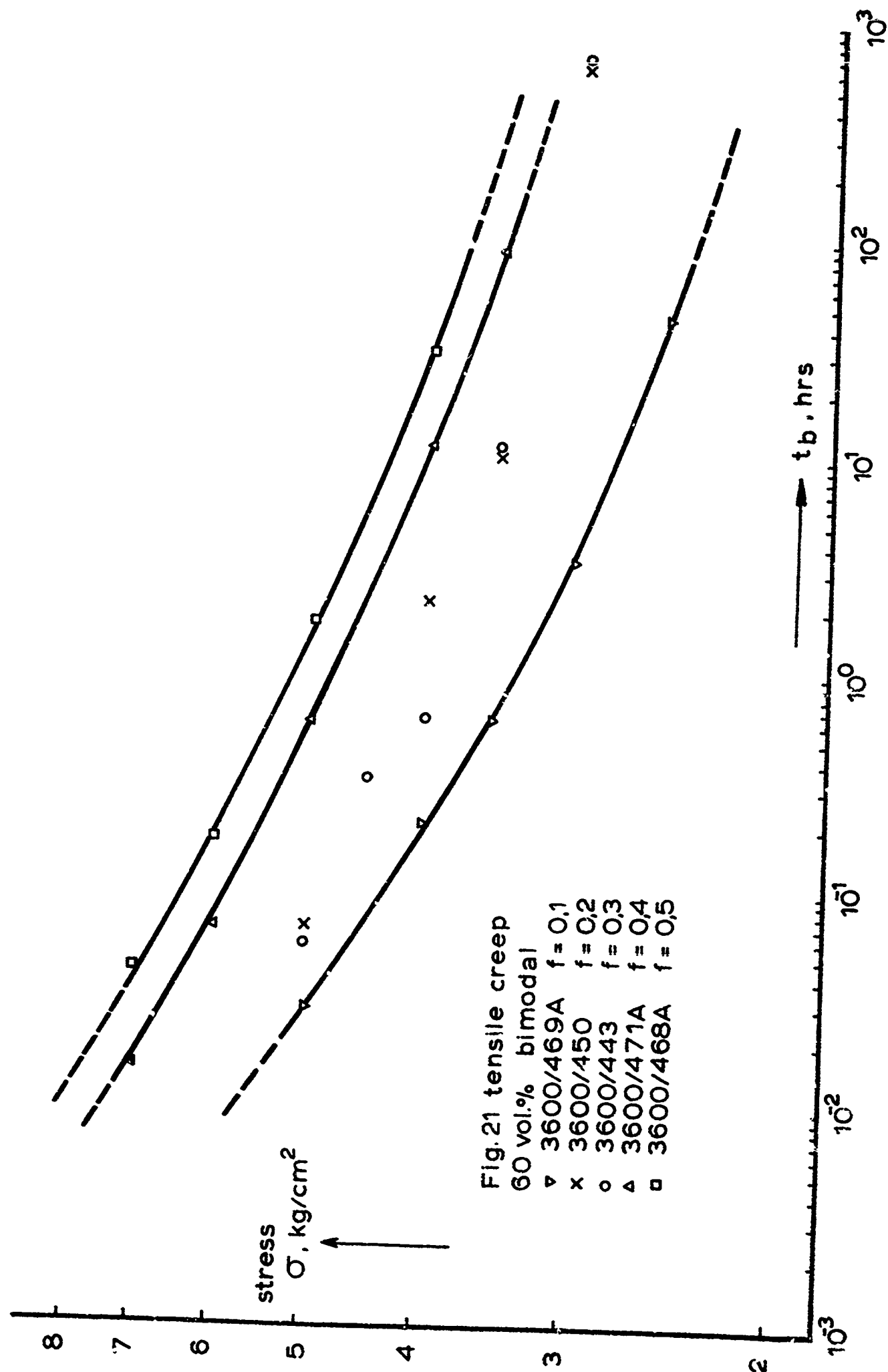


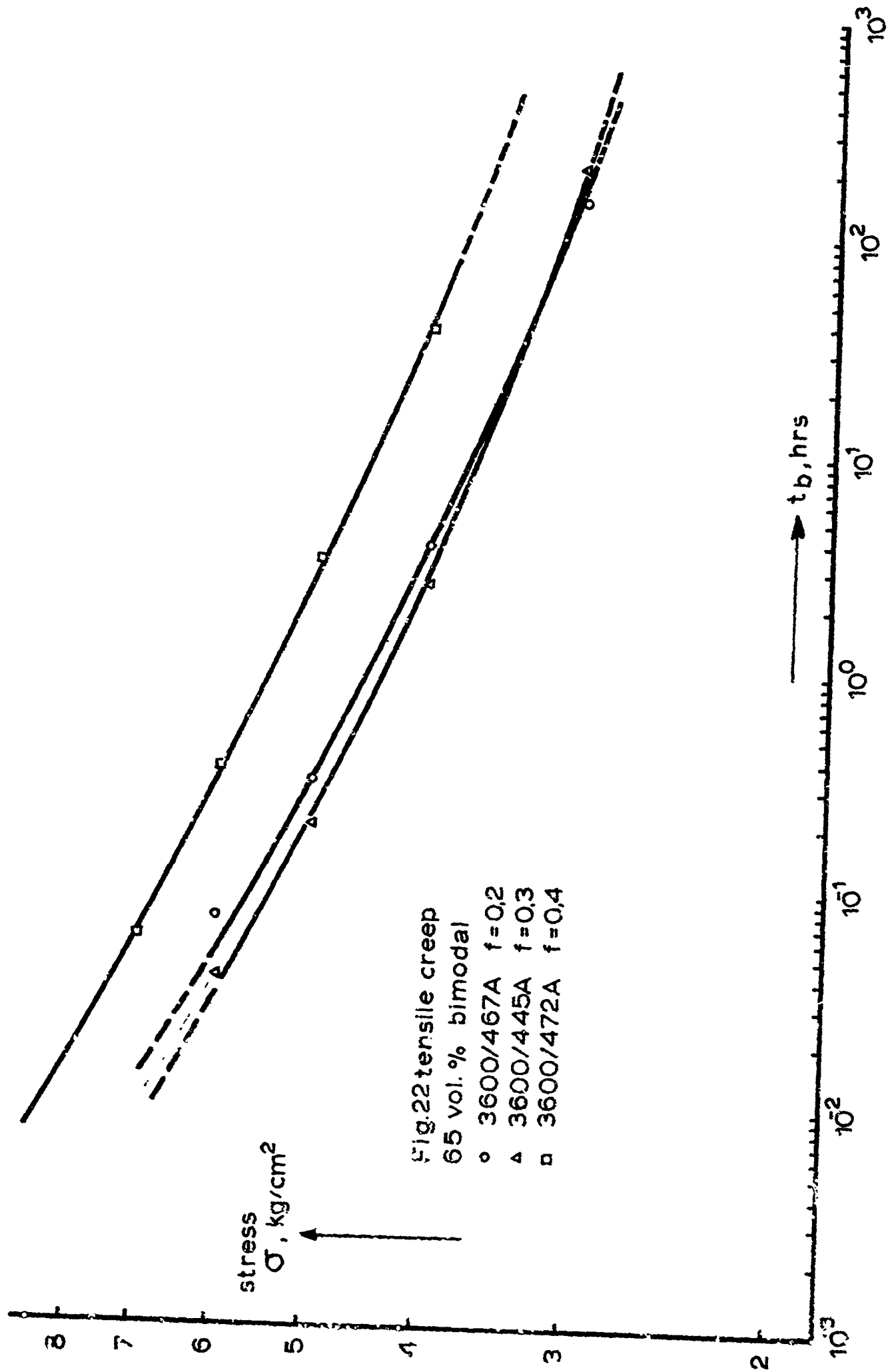
A



→ t , hrs

3





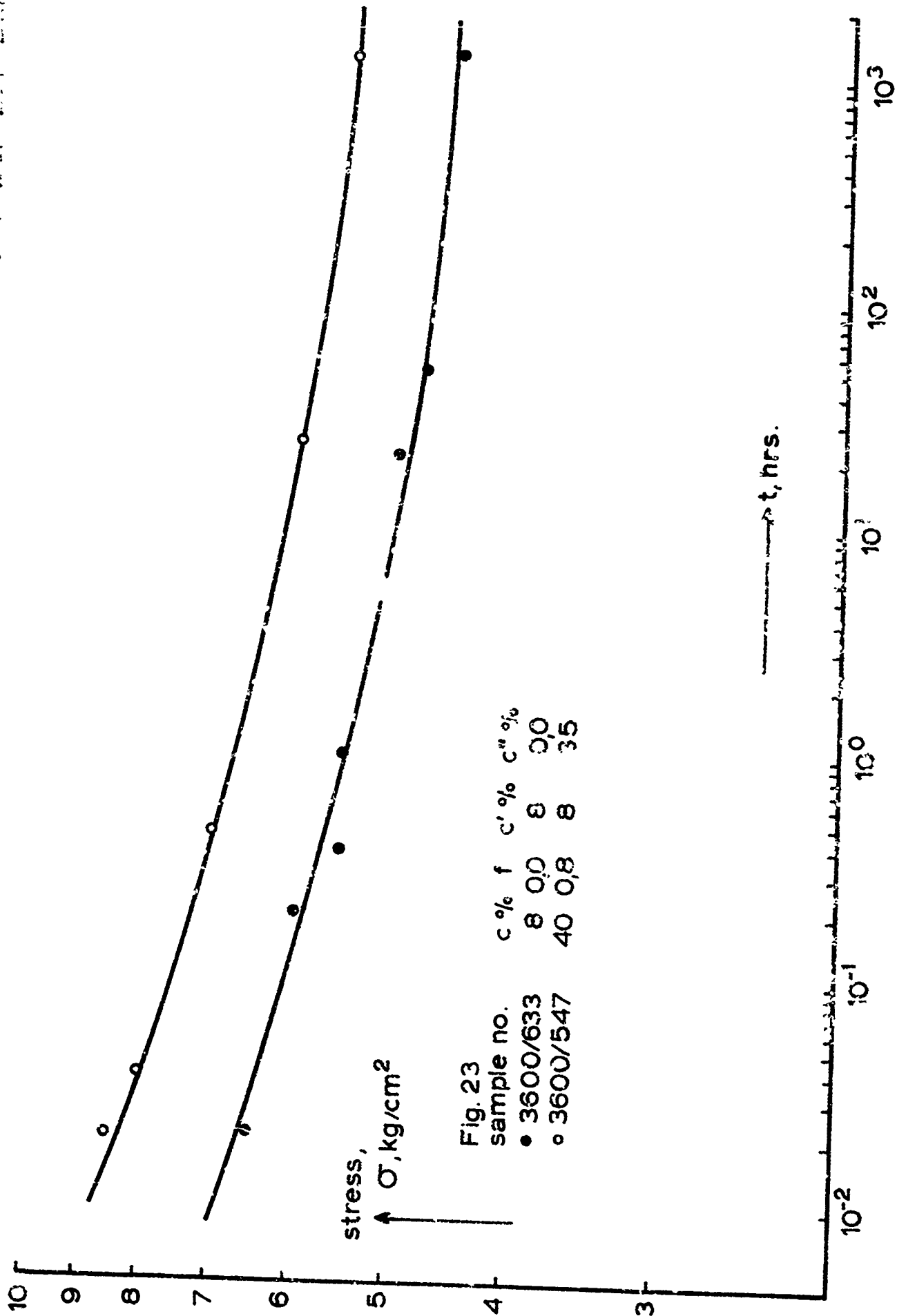


Fig. 23

sample no.

• 3600/633

○ 3600/547

c %

8 0,0

40 0,8

f

0,0

0,8

c' %

8

8

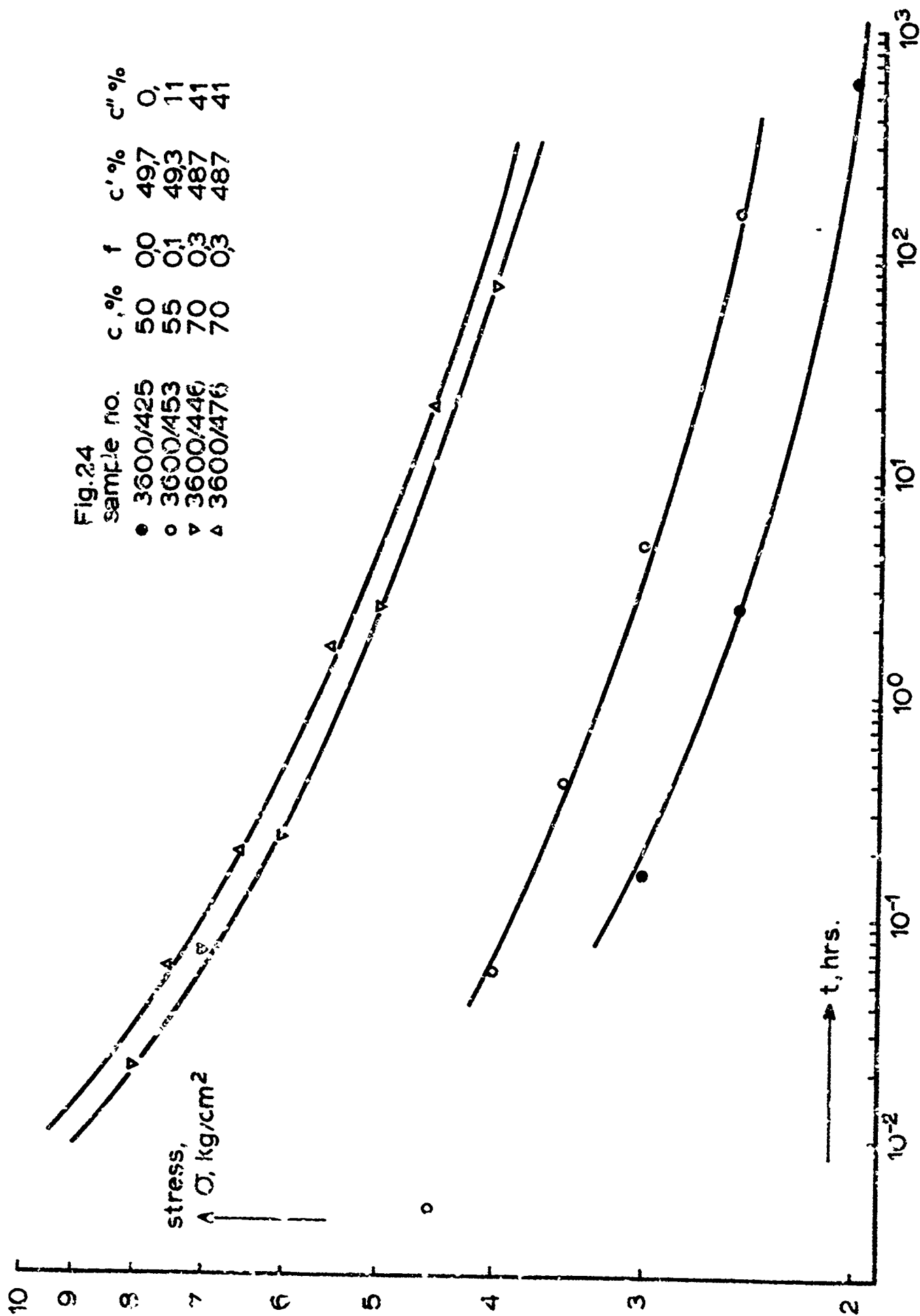
c'' %

0,0

3,5

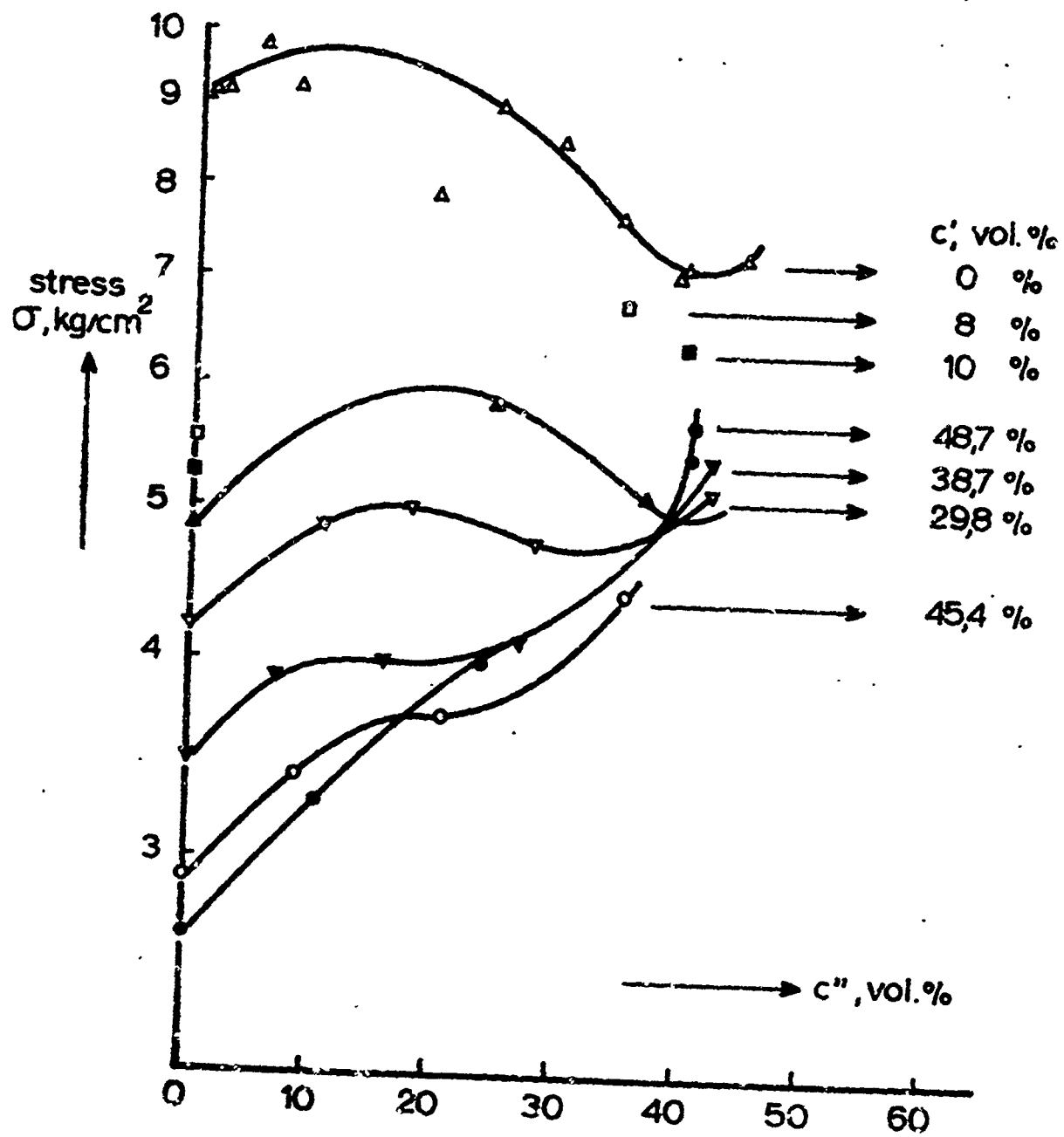
Fig. 24

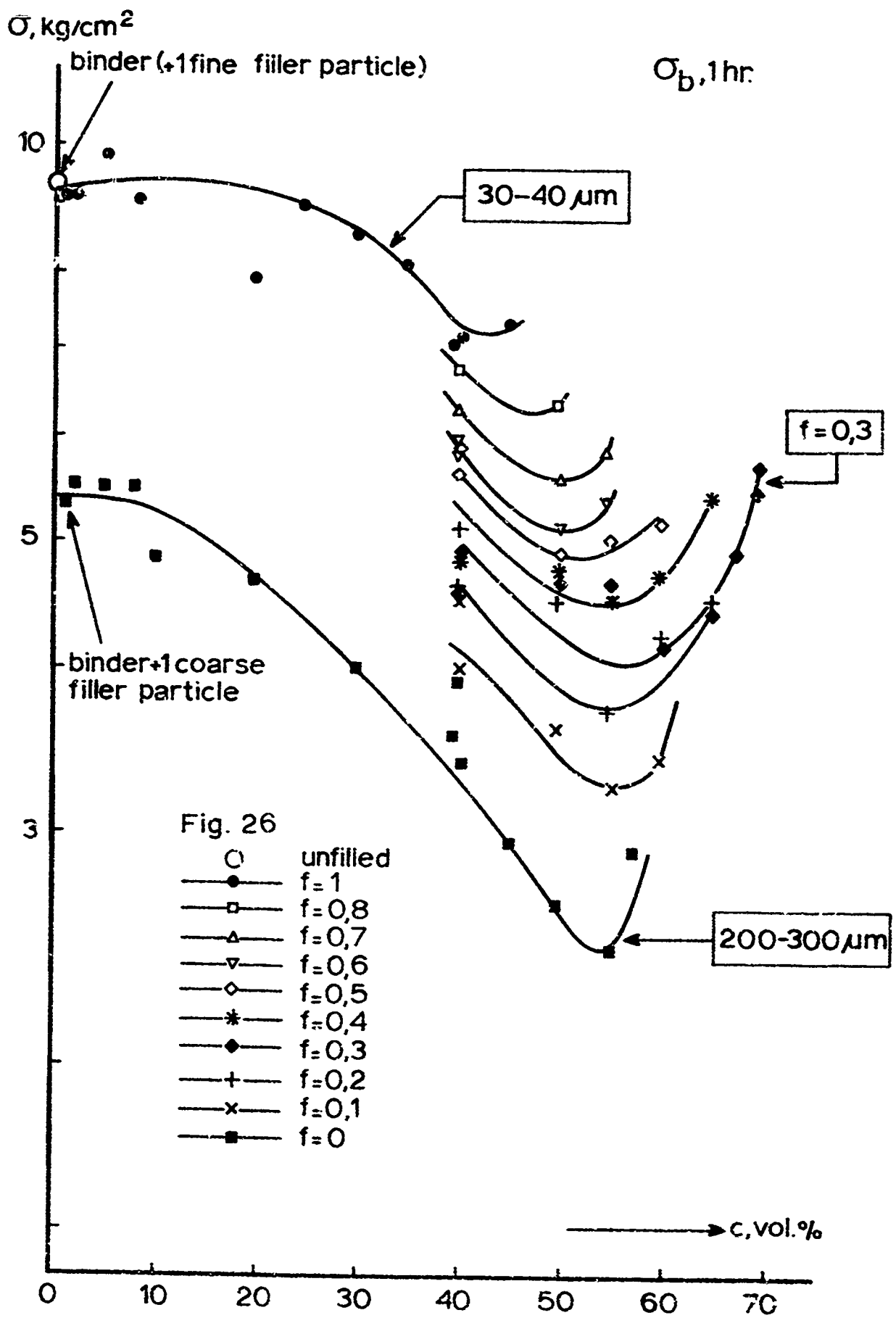
sample no.	c, %	f	c', %	c'', %
● 3600/425	50	0,0	49,7	0,
○ 3600/453	55	0,1	49,3	11
▽ 3600/446	70	0,3	48,7	41
△ 3600/476	70	0,3	48,7	41

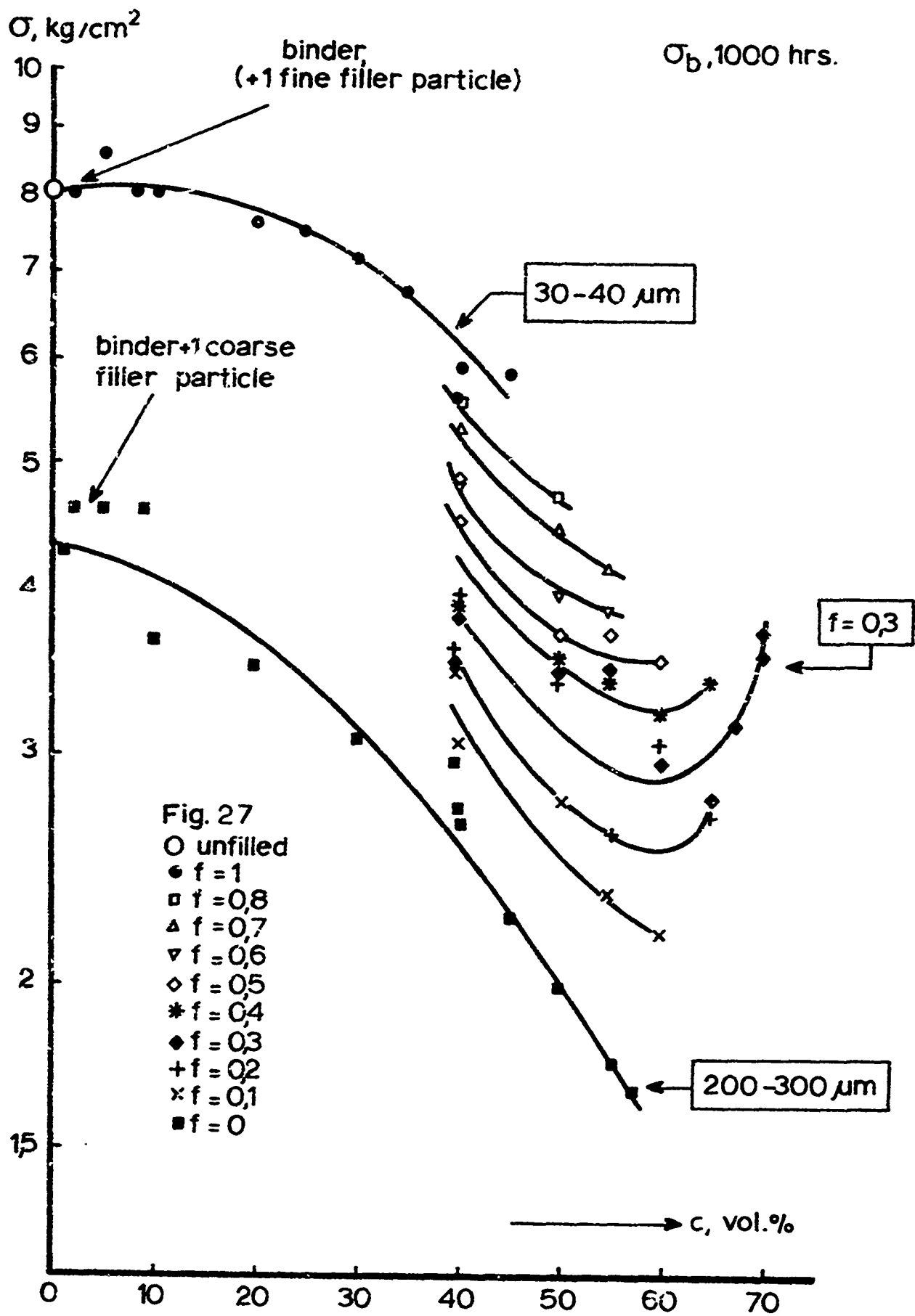


σ , 1 hr.

Fig. 25







Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Central Laboratory TNO - Delft Netherlands		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Mechanical Properties of Highly Filled Elastomers VIII. Rupture properties of the composite system polyurethane rubber-sodium chloride at room temperature.			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report No. 8			
5. AUTHOR(S) (First name, middle initial, last name) Schwarzl, Friedrich R. Bree, Hendricus W.			
6. REPORT DATE December 1969		7a. TOTAL NO. OF PAGES 54	7b. NO. OF REFS 15
8a. CONTRACT OR GRANT NO. F 6/052 67 C 0059		9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report No. 8	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) CL 69/197	
c.			
d.			
10. DISTRIBUTION STATEMENT Distribution list for unclassified technical reports			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Office of Naval Research	
13. ABSTRACT <p>A large number of composites has been prepared with sodium chloride as a filler and polyurethane rubber as a binder. Two filler sizes were used, viz a coarse filler fraction of 200 - 300 μm and a fine filler fraction of 30 - 40 μm. Furthermore a bimodal filler was prepared by mixing those fractions in ratios, which were varied between 0,1 and 0,9 in steps of 0,1. Composites were prepared which contained between 1 vol % and 58 vol % of coarse filler, between 1 vol % and 45 vol % of fine filler, and between 40 vol % and 70 vol % of bimodal filler of different compositions.</p> <p>Those materials were investigated in tensile creep under dead loads at 21 °C and 65 % P.H. The creep behaviour (devetting transition) was measured, the relation between tensile strength and rupture time was determined, and rupture surfaces were studied by microscope and microscan.</p>			

DD FORM 1473 (PAGE 1)
1 NOV 65
S/N 0101-807-6811

Unclassified

Security Classification

A-31408

Unclassified

Security Classification

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KEY WORDS

LINK A

LINK B

LINK C

ROLE

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WT

Polyurethane rubber
Dummy propellant
Filler content
Filler size
Filler size distribution
Bimodal filled systems
Creep
Strength

DD FORM 1473 (BACK)
1 NOV 65

DA FORM 101-107-101

Unclassified

Security Classification

A-31409